Photoinduced Cu-catalysed asymmetric amidation via ligand cooperativity

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Supplementary Information

Table of Contents

I. General Information

All reactions were performed under an atmosphere of dry nitrogen. Anhydrous *i*-Pr_2O and 2-Me-THF were purchased from Sigma-Aldrich and stored under nitrogen; other solvents were purified by passage through activated aluminum oxide in a solvent-purification system. $Cu(CH_3CN)_4PF_6$ (Strem, >98%), enantiopure 2,2'-bis[di(3,5-di-*t*-butylphenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl (Strem, 97%; **P**), enantiopure *N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethylenediamine (Sigma-Aldrich, 97%; **N2***), and all other commercially available materials were used as received. Racemic 2,2'-bis[di(3,5-di-*t*-butylphenyl)phosphino]-6,6'-dimethoxy-1,1'-biphenyl (**P**) was prepared following a literature procedure.[1]

^{1}H, ^{13}C, ^{31}P and ^{19}F NMR data were collected on a Bruker 400 MHz or a Varian 300 or 500 MHz spectrometer at ambient temperature unless otherwise noted. HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 5 μm). SFC analyses were carried out on an Agilent 1260 Infinity II system with Daicel CHIRALPAK® or Daicel CHIRALCEL® columns (4.6 × 250 mm, particle size 5 μm). FT-IR measurements were carried out on a Thermo Scientific Nicolet iS5 FT-IR spectrometer equipped with an iD5 ATR accessory. Optical rotation data were obtained with a Jasco P-2000 polarimeter at 589 nm and at 22–24 °C, using a 100 mm path-length cell in the solvent and at the concentration indicated. LRMS were acquired using an Agilent 6200 Series TOF MS with an Agilent G1978A Multimode source in electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) mode. Blue LED lamps (PR 440 nm, Kessil) were used to irradiate the reaction mixtures. Flash column chromatography was performed using silica gel (SiliaFlash® P60, particle size 40–63 μm, Silicycle).

X-ray crystallography studies were carried out in the Beckman Institute Crystallography Facility on a Bruker APEX-II CCD diffractometer with filtered Cu-Kα radiation or Mo-Kα radiation. Suitable single crystals for X-ray structure determination were selected from the mother liquor and mounted in a nylon loop in immersion oil. The structures were solved and refined using APEX 3 software. Structure solution was performed using the SHELXT structure solution program using direct methods. Refinement was performed using the SHELXL refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters. All C–H hydrogen atoms were refined isotropically on calculated positions by using a riding model with their U_{iso} values constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other atoms.

Steady-state fluorimetry and time-resolved luminescence measurements were performed in the Beckman Institute Laser Resource Center. Steady-state emission spectra were collected on a Jobin S4 Yvon Spec Fluorolog-3-11 with a Hamamatsu R928P photomultiplier tube detector with photon counting. Absorbance spectra were acquired on a Cary 50 UV-Vis spectrophotometer. For luminescence at the nanosecond to microsecond time scale, a Q-switched Nd:YAG laser (Spectra-Physics QuantaRay PRO-Series; 355 nm; pulse duration 8 ns,

operating at 10 Hz) was used as the source of the excitation pulse, with laser power at 0.5 mJ/pulse.

X-band EPR measurements were conducted with a Bruker EMX spectrometer at 77 K. Simulation of EPR data was obtained using EasySpin software.

ESI–MS data were collected using an Agilent 6200 Series TOF MS with Agilent G1978A multimode source in electrospray ionization mode. HRMS data were acquired using an Agilent 1260 Infinity II Series TOF MS system. Melting points were measured using a Büchi melting point B-545 instrument.

II. Preparation of N1* and CsOPh·H_2O

The yields have not been optimized.

Preparation of *N,N*-dimethyl-1,2-bis(4-(trifluoromethyl)phenyl)ethane-1,2-diamine (N1*). In accordance with a literature procedure,[2] under a nitrogen atmosphere, a three neck round-bottom flask (500 mL) was charged with Zn dust (325 mesh; 19.6 g, 300 mmol) and anhydrous acetonitrile (75 mL). To activate the Zn, 1,2-dibromoethane (5.25 g, 28 mmol) was added, and the mixture was brought to reflux for 1 min, then allowed to cool to room temperature; next, a small amount of TMSCl (4.8 mL, 38 mmol) was added, whereupon the evolution of gas (ethylene) was observed. The mixture was stirred for 45 min, and then a solution of *N*-methyl-1-(4-(trifluoromethyl)phenyl)methanimine (56.2 g, 300 mmol) in acetonitrile (150 mL) was added in one portion. TMSCl (57 mL, 450 mmol) was added slowly at a rate to maintain the internal temperature below 35–40 °C. After completion of the addition, the mixture was stirred for 1 h, and then it was cooled to 0 °C and cautiously hydrolyzed with a mixture of aqueous NH_4OH (90 mL) and a saturated aqueous solution of NH_4Cl (200 mL). The excess Zn was removed by filtration, the organic phase was separated, and the aqueous phase extracted with CH_2Cl_2 (3x150 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator, resulting in a semi-solid residue. The diamine was dissolved in absolute EtOH (600 mL), and racemic tartaric acid (150 mmol, 22.2 g) was added. The heterogeneous mixture was brought to reflux for 30 min. After cooling to room temperature, the precipitate was collected by filtration and washed twice with EtOH (2x70 mL). To the obtained precipitate was then added EtOH (200 mL), and the heterogeneous mixture was brought to reflux again for 30 min. After cooling to room temperature, the precipitate was collected by filtration and washed twice with EtOH (2x30 mL). The precipitate was poured into a mixture of an aqueous solution of 35% NaOH (100 mL) and Et_2O (200 mL). The resulting mixture was stirred for 30 min, and then the phases were separated. The aqueous phase was extracted with Et_2O (3x150 mL), and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford pure *d,l*-diamine ligand **N1** (18.0 g, 32% yield).

(*L*)-Tartaric acid (7.18 g, 47.9 mmol) was added to pure *d,l*-diamine ligand **N1** (18.0 g, 47.9 mmol) in EtOH (200 mL), and the resulting mixture was refluxed for 30 min. After cooling to room temperature, the precipitate was collected by filtration and washed with EtOH (2x10 mL), while the mother liquor was set aside. EtOH (100 mL) was added to the precipitate, and the resulting mixture was refluxed again for 30 min. After cooling to room temperature, the precipitate was collected by filtration and washed with EtOH (2x10 mL). The precipitate was added to a mixture of an aqueous solution of 35% NaOH (60 mL) and Et_2O (200 mL). The resulting mixture was stirred for 30 min, and the phases were separated. The aqueous phase was extracted with Et_2O (3x100 mL), and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the enantiopure (*R,R*)-**N1*** (8.13 g, >99% ee) as a white solid.

The combined mother liquor was concentrated. To the residue was added an aqueous solution of 35% NaOH (100 mL) and Et_2O (200 mL). The mixture was then stirred for 30 min, and the phases were separated. The aqueous phase was extracted with Et_2O (3x100 mL), and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. To the residue in EtOH (200 mL) was added (*D*)-tartaric acid (3.90 g, 26 mmol), and the resulting mixture was refluxed for 30 min. After cooling to room temperature, the precipitate was collected by filtration and washed with EtOH (2x10 mL). To the obtained precipitate was added EtOH (100 mL), and the resulting mixture was again refluxed for 30 min. After cooling to room temperature, the precipitate was collected by filtration and washed with EtOH (2x10 mL). The precipitate was added to a mixture of an aqueous solution of 35% NaOH (60 mL) and Et_2O (200 mL). The resulting mixture was stirred for 30 min, and the phases were separated. The aqueous phase was extracted with Et_2O (3 x 100 mL), and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator to afford enantiopure (*S,S*)-**N1*** (9.05 g, >99% ee) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 4H), 7.16 (d, *J* = 8.0 Hz, 4H), 3.62 (s, 2H), 2.27 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 129.5 (q, *J* = 32.3 Hz), 128.2, 125.1 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.1 Hz), 70.8, 34.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.5.

FT-IR (film) 3333, 2948, 2800, 1620, 1416, 1326, 1163, 1121, 1067, 1018, 833, 772, 613 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{18}H_{19}F_6N_2$: 377.1447, found: 377.1441.

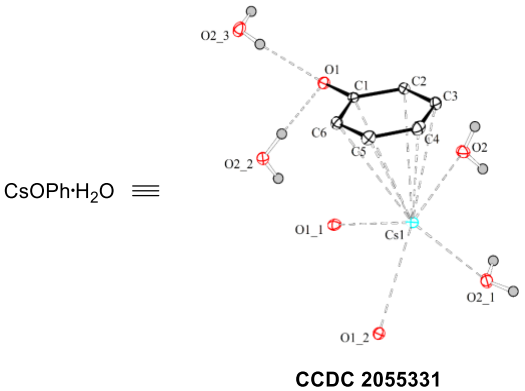
$[\alpha]^{24}_D$ = –51 (*c* 1.5, $CHCl_3$).

m.p.: 46 °C.

To determine the ee, (*S,S*)-**N1*** was converted to *N,N'*-(1,2-bis(4-(trifluoromethyl) phenyl)ethane-1,2-diyl)bis(*N*-methylbenzamide) by reaction with benzoyl chloride in the presence of Et_3N and a catalytic amount of DMAP. The ee of *N,N'*-(1,2-bis(4-(trifluoromethyl) phenyl)ethane-1,2-diyl)bis(N-methylbenzamide) was determined via HPLC on a CHIRALPAK AD-H column (20% *i*-PrOH in hexanes, 1.0 mL/min); retention times: (*S,S*)-**N1***, 14.9 min, (*R,R*)-**N1***, 18.2 min.

Preparation of CsOPh·H_2O. Under a nitrogen atmosphere, a three neck round-bottom flask (500 mL) was charged with CsOH·H_2O (20.0 g, 119 mmol), phenol (11.8 g, 125 mmol), and anhydrous toluene (250 mL), and then a Dean-Stark apparatus was added. The resulting mixture was heated to reflux for 8 h. As water was removed by the Dean-Stark apparatus, a white precipitate appeared. The mixture was cooled to room temperature, and the white precipitate was filtered and washed with anhydrous toluene (2x30 mL) in a glovebox to give anhydrous CsOPh. To the anhydrous CsOPh, anhydrous THF (300 mL) was added, and the resulting mixture was heated to 60 °C. Water (2.14 g, 119 mmol) was added in one portion, causing the CsOPh to immediately dissolve. The mixture was further stirred for 1 h, and then it was cooled to room temperature. The colorless crystals that formed were filtered and

washed with THF (2x15 mL) in a glovebox to afford CsOPh·H_2O (26.8 g, 92% yield). The CsOPh·H_2O crystal was ground into a fine powder for further use.



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Thermal ellipsoid plot of CsOPh·H_2O at 50% probability level. The O-H hydrogen atoms were found in the residual density map and refined isotropically. Additional water molecules (O2_X) and oxygen atoms (O1_X) that are not included in the asymmetric unit are given to show the coordination sphere of the metal. C–H Hydrogen atoms are not shown for clarity.

Data collection and structure refinement of CsOPh·H_2O

Identification code	d19042	
Chemical formula	$C_6H_7CsO_2$	
Formula weight	244.03 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.135 x 0.183 x 0.259 mm	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 6.9696(5) Å	α = 90°
	b = 10.9227(7) Å	β = 90°
	c = 19.3516(13) Å	γ = 90°
Volume	1473.18(17) $Å^3$	
Z	8	
Density (calculated)	2.200 g/cm^3	
Absorption coefficient	4.952 mm^{-1}	
F(000)	912	

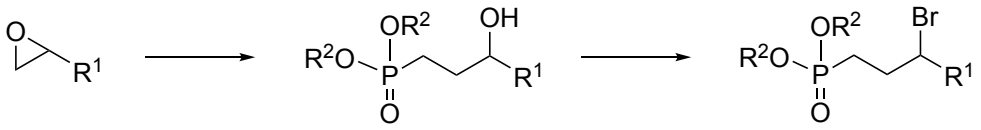
Theta range for data collection	3.60 to 36.31°

Index ranges	-11<=h<=11, -18<=k<=18, -32<=l<=32
Reflections collected	103033
Independent reflections	3571 [R(int) = 0.0334]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3571 / 0 / 90
Goodness-of-fit on F^2	1.131
Δ/σ_{max}	0.004
Final R indices	3243 data; I>2σ(I) R1 = 0.0143, wR2 = 0.0318
	all data R1 = 0.0174, wR2 = 0.0328
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0133P)^2+0.9690P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.690 and -1.480 eÅ^{-3}
R.M.S. deviation from mean	0.103 eÅ^{-3}

III. Preparation of Electrophiles and Nucleophiles

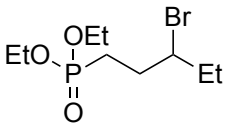
The yields have not been optimized.

General Procedure 1 (GP-1) for the synthesis of γ-bromophosphonates.



The γ-hydroxyphosphonates were synthesized following a literature procedure.[3]

Imidazole (1.2 equiv) and PPh_3 (1.2 equiv) were dissolved in CH_2Cl_2 ([imidazole] = 0.20 M), and the resulting solution was cooled to 0 °C. At this temperature, bromine (1.2 equiv) was added dropwise over 10 min, and the resulting mixture was stirred for 10 min. The γ-hydroxyphosphonate (1.0 equiv) was added, and the resulting mixture was allowed to warm to room temperature and stir overnight. Next, water (half of the volume of CH_2Cl_2) was added to the reaction mixture. The organic layer was then separated, and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were concentrated. To the residue was added hexane/Et_2O (5/1; for hexane: 10 mL/mmol of γ-hydroxyphosphonate). The resulting mixture was stirred for 15 min, and then it was filtered. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel to afford the pure product.



Diethyl (3-bromopentyl)phosphonate. The title compound was synthesized according to **GP-1** from diethyl (3-hydroxypentyl)phosphonate (18.0 g, 80.3 mmol) and purified by flash column chromatography on silica gel (acetonitrile as eluent). 12.3 g (42.8 mmol, 53% yield). Colorless oil.

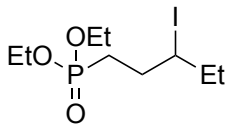
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.21 – 4.06 (m, 4H), 4.06 – 3.98 (m, 1H), 2.24 – 2.00 (m, 3H), 1.93 – 1.83 (m, 3H), 1.36 (t, *J* = 7.1 Hz, 6H), 1.08 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 61.7 (d, *J* = 6.5 Hz), 61.6 (d, *J* = 6.5 Hz), 59.7 (d, *J* = 18.3 Hz), 32.0, 31.7 (d, *J* = 3.8 Hz), 24.1 (d, *J* = 142.1 Hz), 16.4 (d, *J* = 5.9 Hz), 12.0.

^{31}P NMR (121 MHz, $CDCl_3$) δ 31.0.

FT-IR (film) 3470, 2977, 1651, 1440, 1392, 1241, 1024, 967, 802, 749 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_9H_{21}BrO_3P$: 287.0406, found: 287.0402.



Diethyl (3-iodopentyl)phosphonate. To a solution of diethyl (3-bromopentyl)phosphonate (0.79 g, 2.0 mmol) in acetone (20 mL) was added sodium iodide (0.45 g, 6.0 mmol, 3.0 equiv).

The resulting suspension was stirred at room temperature for 24 h, and then it was filtered, and the filtrate was concentrated. The residue was dissolved in ethyl acetate (100 mL), and the resulting solution was washed with an aqueous solution of $Na_2S_2O_3$ (50 mL x 2), dried, and concentrated to afford the desired product as a pale yellow oil. 0.65 g, 97% yield.

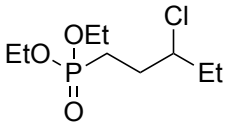
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 – 3.95 (m, 5H), 2.09 – 1.89 (m, 3H), 1.87 – 1.63 (m, 3H), 1.27 (t, *J* = 7.1 Hz, 6H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 61.7 (d, *J* = 6.5 Hz), 61.6 (d, *J* = 6.5 Hz), 41.4 (d, *J* = 19.2 Hz), 33.6, 33.2 (d, *J* = 3.7 Hz), 26.1 (d, *J* = 141.6 Hz), 16.5 (d, *J* = 6.0 Hz), 14.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.7.

FT-IR (film) 3462, 2976, 1243, 1028, 961, 791 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_9H_{21}IO_3P$: 335.0268, found: 335.0267.



Diethyl (3-chloropentyl)phosphonate. A solution of $SOCl_2$ (1.43 g, 12 mmol, 1.2 equiv) in chloroform (5.0 mL) was added dropwise to a solution of diethyl (3-hydroxypentyl)phosphonate (2.24 g, 10 mmol) and pyridine (0.95 g, 12 mmol, 1.2 equiv) in chloroform (10 mL) at 0 °C. The resulting solution was allowed to warm to room temperature, and then it was heated to 60 °C for 8 h. After cooling to room temperature, the resulting mixture was concentrated. The residue was dissolved in CH_2Cl_2 (150 mL) and washed with an aqueous solution of $NaHCO_3$ (50 mL x 2), dried, and concentrated. The residue was purified by flash column chromatography on silica gel (66% EtOAc/CH_2Cl_2) to afford the desired product as a colorless oil. 1.33 g, 55% yield.

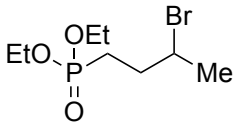
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 – 4.04 (m, 4H), 3.91 – 3.84 (m, 1H), 2.15 – 1.61 (m, 6H), 1.34 (t, *J* = 7.1 Hz, 6H), 1.04 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 65.4 (d, *J* = 18.0 Hz), 61.6 (d, *J* = 6.4 Hz), 61.5 (d, *J* = 6.4 Hz), 31.3, 31.0 (d, *J* = 4.0 Hz), 22.9 (d, *J* = 142.4 Hz), 16.5 (d, *J* = 6.0 Hz), 10.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 31.3.

FT-IR (film) 3479, 2977, 1443, 1392, 1241, 1030, 815 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_9H_{21}ClO_3P$: 243.0911, found: 243.0909.



Diethyl (3-bromobutyl)phosphonate. The title compound was synthesized according to **GP-1** from diethyl (3-hydroxybutyl)phosphonate (5.30 g, 25.2 mmol) and purified by flash column chromatography on silica gel (acetonitrile as eluent). 4.56 g (16.7 mmol, 66% yield). Colorless oil.

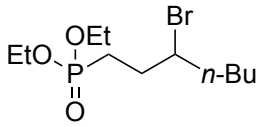
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.24 – 4.02 (m, 5H), 2.18 – 1.98 (m, 3H), 1.92 – 1.80 (m, 1H), 1.75 (d, *J* = 6.6 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 61.7 (d, *J* = 6.5 Hz), 61.6 (d, *J* = 6.5 Hz), 51.1 (d, *J* = 19.1 Hz), 33.9 (d, *J* = 3.9 Hz), 26.1, 24.2 (d, *J* = 142.3 Hz), 16.4 (d, *J* = 5.9 Hz).

^{31}P NMR (121 MHz, $CDCl_3$) δ 30.9.

FT-IR (film) 3456, 2983, 1651, 1444, 1392, 1249, 1025, 966, 791, 750 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_8H_{19}BrO_3P$: 273.0250, found: 273.0248.



Diethyl (3-bromoheptyl)phosphonate. The title compound was synthesized according to **GP-1** from diethyl (3-hydroxyheptyl)phosphonate (5.05 g, 20.0 mmol) and purified by flash column chromatography on silica gel (acetonitrile as eluent). 4.27 g (13.5 mmol, 68% yield). Colorless oil.

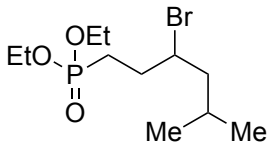
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.38 – 3.69 (m, 5H), 2.20 – 1.97 (m, 3H), 1.91 – 1.73 (m, 3H), 1.56 – 1.46 (m, 1H), 1.46 – 1.26 (m, 9H), 0.91 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 61.7 (d, *J* = 6.5 Hz), 61.6 (d, *J* = 6.5 Hz), 58.1 (d, *J* = 18.6 Hz), 38.7, 32.0 (d, *J* = 3.8 Hz), 29.7, 24.0 (d, *J* = 142.1 Hz), 22.1, 16.5 (d, *J* = 6.1 Hz), 13.9.

^{31}P NMR (121 MHz, $CDCl_3$) δ 31.1.

FT-IR (film) 3452, 2957, 1644, 1442, 1392, 1237, 1030, 967, 792, 752 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{11}H_{25}BrO_3P$: 315.0719, found: 315.0717.



Diethyl (3-bromo-5-methylhexyl)phosphonate. The title compound was synthesized according to **GP-1** from diethyl (3-hydroxy-5-methylhexyl)phosphonate (2.41 g, 9.4 mmol) and purified by flash column chromatography on silica gel (acetonitrile as eluent). 1.77 g (5.6 mmol, 60% yield). Colorless oil.

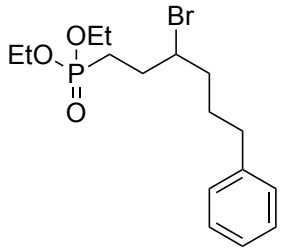
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.23 – 4.06 (m, 5H), 2.24 – 2.15 (m, 1H), 2.14 – 2.00 (m, 2H), 1.99 – 1.84 (m, 3H), 1.56 (ddd, *J* = 14.2, 8.7, 4.5 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 6H), 0.96 (dd, *J* = 22.5, 6.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 61.7 (d, *J* = 6.4 Hz), 61.6 (d, *J* = 6.4 Hz), 56.3 (d, *J* = 18.4 Hz), 47.9, 32.4 (d, *J* = 3.8 Hz), 26.4, 24.0 (d, *J* = 142.1 Hz), 22.8, 21.2, 16.5 (d, *J* = 6.0 Hz).

^{31}P NMR (121 MHz, $CDCl_3$) δ 31.2.

FT-IR (film) 3458, 2959, 1736, 1470, 1392, 1241, 1030, 966, 792, 752 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{11}H_{25}BrO_3P$: 315.0719, found: 315.0721.



Diethyl (3-bromo-6-phenylhexyl)phosphonate. The title compound was synthesized according to **GP-1** from diethyl (3-hydroxy-6-phenylhexyl)phosphonate (2.91 g, 9.3 mmol) and purified by flash column chromatography on silica gel (33% EtOAc/CH_2Cl_2). 1.22 g (3.2 mmol, 35% yield). Colorless oil.

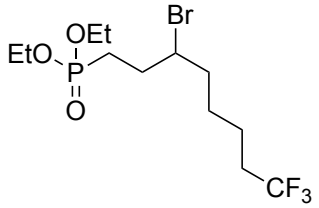
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.26 – 7.19 (m, 3H), 4.24 – 3.99 (m, 5H), 2.79 – 2.59 (m, 2H), 2.25 – 2.02 (m, 3H), 2.01 – 1.76 (m, 5H), 1.38 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 128.39, 128.36, 125.9, 61.7 (d, *J* = 6.4 Hz), 61.6 (d, *J* = 6.4 Hz), 57.6 (d, *J* = 18.6 Hz), 38.3, 35.1, 32.1 (d, *J* = 3.8 Hz), 29.2, 24.1 (d, *J* = 142.2 Hz), 16.5 (d, *J* = 6.0 Hz).

^{31}P NMR (121 MHz, $CDCl_3$) δ 31.0.

FT-IR (film) 3459, 2931, 1603, 1496, 1454, 1392, 1234, 1029, 958, 792, 753, 701 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{27}BrO_3P$: 377.0876, found: 377.0880.



Diethyl (3-bromo-8,8,8-trifluorooctyl)phosphonate. The title compound was synthesized according to **GP-1** from diethyl (8,8,8-trifluoro-3-hydroxyoctyl)phosphonate (4.40 g, 11.5 mmol) and purified by flash column chromatography on silica gel (33% EtOAc/CH_2Cl_2). 3.51 g (9.2 mmol, 80% yield). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.25 – 4.11 (m, 4H), 4.11 – 4.06 (m, 1H), 2.29 – 2.03 (m, 5H), 1.98 – 1.81 (m, 3H), 1.76 – 1.48 (m, 4H), 1.39 (td, *J* = 7.1, 0.8 Hz, 6H).

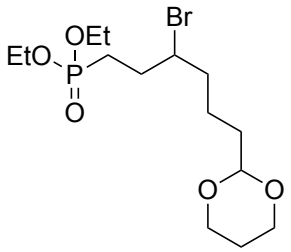
^{13}C NMR (126 MHz, $CDCl_3$) δ 127.0 (q, *J* = 276.3 Hz), 61.7 (d, *J* = 6.5 Hz), 61.6 (d, *J* = 6.5 Hz), 57.1 (d, *J* = 18.3 Hz), 38.5, 33.6 (q, *J* = 28.4 Hz), 32.1 (d, *J* = 3.8 Hz), 26.7, 24.0 (d, *J* = 142.4 Hz), 21.3 (d, *J* = 2.9 Hz), 16.4 (d, *J* = 5.9 Hz).

^{31}P NMR (121 MHz, $CDCl_3$) δ 30.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ –66.5.

FT-IR (film) 3466, 2983, 1644, 1441, 1392, 1233, 1130, 1054, 962, 792, 749, 657 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{12}H_{24}BrF_3O_3P$: 383.0593, found: 383.0600.



Diethyl (3-bromo-6-(1,3-dioxan-2-yl)hexyl)phosphonate. The title compound was synthesized according to **GP-1** from diethyl (6-(1,3-dioxan-2-yl)-3-hydroxyhexyl)phosphonate (3.58 g, 11.0 mmol) and purified by flash column chromatography on silica gel (33% EtOAc/CH_2Cl_2). 3.05 g (7.9 mmol, 72% yield). Colorless oil.

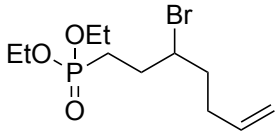
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.54 (t, *J* = 4.5 Hz, 1H), 4.23 – 3.95 (m, 7H), 3.77 (t, *J* = 12.5 Hz, 2H), 2.20 – 2.00 (m, 4H), 1.91 – 1.82 (m, 4H), 1.70 – 1.51 (m, 5H), 1.36 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 101.9, 66.9, 61.7 (dd, *J* = 6.4, 3.6 Hz), 57.6 (d, *J* = 18.8 Hz), 38.7, 34.4, 32.0 (d, *J* = 3.8 Hz), 25.8, 24.0 (d, *J* = 142.1 Hz), 22.1, 16.4 (d, *J* = 5.9 Hz).

^{31}P NMR (121 MHz, $CDCl_3$) δ 31.0.

FT-IR (film) 3456, 2958, 1651, 1440, 1392, 1239, 1145, 1025, 961, 813, 722 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{29}BrO_5P$: 387.0930, found: 387.0931.



Diethyl (3-bromohept-6-en-1-yl)phosphonate. The title compound was synthesized according to **GP-1** from diethyl (3-hydroxyhept-6-en-1-yl)phosphonate (4.30 g, 17.2 mmol) and purified by flash column chromatography on silica gel (acetonitrile as eluent). 2.88 g (9.2 mmol, 53% yield). Colorless oil.

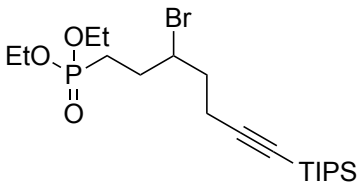
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.85 – 5.73 (m, 1H), 5.16 – 4.99 (m, 2H), 4.25 – 3.96 (m, 5H), 2.44 – 2.30 (m, 1H), 2.29 – 1.81 (m, 7H), 1.37 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 115.8, 61.7 (d, *J* = 6.4 Hz), 61.6 (d, *J* = 6.4 Hz), 57.0 (d, *J* = 18.2 Hz), 37.9, 32.1 (d, *J* = 3.8 Hz), 31.6, 24.0 (d, *J* = 142.3 Hz), 16.4 (d, *J* = 5.9 Hz).

^{31}P NMR (121 MHz, $CDCl_3$) δ 30.9.

FT-IR (film) 3456, 2958, 1652, 1440, 1393, 1239, 1146, 1025, 961, 813, 723 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{11}H_{23}BrO_3P$: 313.0563, found: 313.0564.



Diethyl (3-bromo-7-(triisopropylsilyl)hept-6-yn-1-yl)phosphonate. The title compound was synthesized according to **GP-1** from diethyl (3-hydroxy-7-(triisopropylsilyl)hept-6-yn-1-

yl)phosphonate (5.21 g, 12.9 mmol) and purified by flash column chromatography on silica gel (acetonitrile as eluent). 3.04 g (6.5 mmol, 50% yield). Colorless oil.

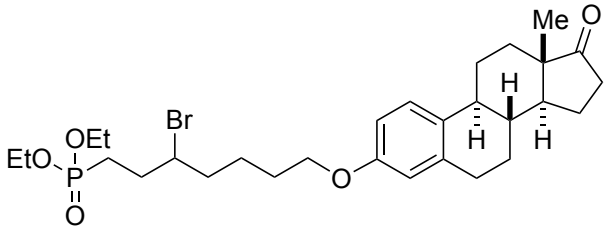
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.27 – 4.20 (m, 1H), 4.20 – 4.09 (m, 4H), 2.57 – 2.50 (m, 2H), 2.27 – 2.03 (m, 4H), 1.94 – 1.81 (m, 1H), 1.38 (td, *J* = 7.1, 1.1 Hz, 6H), 1.21 – 1.00 (m, 22H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 106.6, 81.7, 61.7 (d, *J* = 6.3 Hz), 61.6 (d, *J* = 6.3 Hz), 56.1 (d, *J* = 20.1 Hz), 37.8, 32.0 (d, *J* = 3.7 Hz), 24.1 (d, *J* = 142.4 Hz), 18.62 (d, *J* = 0.6 Hz), 18.57, 16.48 (d, *J* = 6.0 Hz), 16.47 (d, *J* = 6.0 Hz), 11.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.7.

FT-IR (film) 3469, 2942, 2172, 1654, 1462, 1237, 1058, 966, 883, 824, 674 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{20}H_{41}BrO_3PSi$: 467.1740, found: 467.1740.



Diethyl (3-bromo-7-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)heptyl)phosphonate. The title compound was synthesized according to **GP-1** from diethyl (3-hydroxy-7-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)oxy)heptyl)phosphonate (2.95 g, 5.2 mmol) to give diethyl (3-bromo-7-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenan-threne-17,2'-[1,3]dioxolan]-3-yl)oxy)heptyl)phosphonate (purified by flash column chromatography on silica gel; acetonitrile as eluent; 2.10 g, 3.3 mmol, 63% yield), followed by deprotection in aqueous HCl (2.0 M, 10 mL) and THF (50 mL) at room temperature for 4 h. 1.93 g (3.3 mmol, 99% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.63 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 4.12 – 3.93 (m, 5H), 3.87 (t, *J* = 6.1 Hz, 2H), 2.84 – 2.80 (m, 2H), 2.43 (dd, *J* = 18.9, 8.4 Hz, 1H), 2.35 – 2.27 (m, 1H), 2.21 – 2.15 (m, 1H), 2.13 – 1.62 (m, 13H), 1.61 – 1.32 (m, 7H), 1.26 (t, *J* = 7.1 Hz, 6H), 0.84 (s, 3H).

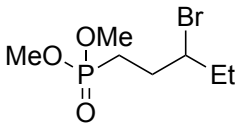
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0, 137.8, 132.0, 126.3, 114.5, 112.1, 67.5, 61.7 (d, *J* = 6.6 Hz), 61.6 (d, *J* = 6.6 Hz), 57.7 (d, *J* = 18.5 Hz), 50.4, 48.0, 44.0, 38.6, 38.4, 35.9, 32.1 (d, *J* = 3.9 Hz), 31.6, 29.7, 28.7, 26.6, 25.9, 24.3, 24.1 (d, *J* = 142.2 Hz), 21.6, 16.5 (d, *J* = 6.1 Hz), 13.9.

^{31}P NMR (121 MHz, $CDCl_3$) δ 31.0.

FT-IR (film) 3454, 2930, 1738, 1608, 1500, 1281, 1247, 1028, 963, 819, 752 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{29}H_{45}BrO_5P$: 583.2183, found: 583.2182.

m.p.: 67-69 °C.



Dimethyl (3-bromopentyl)phosphonate. The title compound was synthesized according to **GP-1** from dimethyl (3-hydroxypentyl)phosphonate (5.45 g, 27.8 mmol) and purified by flash column chromatography on silica gel (acetonitrile as eluent). 3.47 g (13.4 mmol, 48% yield). Colorless oil.

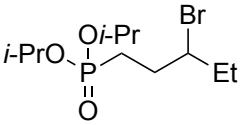
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.96 – 3.87 (m, 1H), 3.69 (d, *J* = 10.8 Hz, 6H), 2.14 – 1.91 (m, 3H), 1.89 – 1.70 (m, 3H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 59.7 (d, *J* = 18.4 Hz), 52.5 (d, *J* = 6.5 Hz), 52.4 (d, *J* = 6.5 Hz), 32.1, 31.6 (d, *J* = 3.9 Hz), 23.1 (d, *J* = 142.1 Hz), 12.1.

^{31}P NMR (121 MHz, $CDCl_3$) δ 33.7.

FT-IR (film) 3456, 2958, 1651, 1456, 1243, 1047, 832, 750 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_7H_{17}BrO_3P$: 259.0093, found: 259.0096.



Diisopropyl (3-bromopentyl)phosphonate. The title compound was synthesized according to **GP-1** from diisopropyl (3-hydroxypentyl)phosphonate (3.33 g, 13.2 mmol) and purified by flash column chromatography on silica gel (acetonitrile as eluent). 2.67 g (8.5 mmol, 64% yield). Colorless oil.

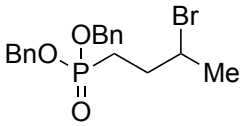
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 – 4.70 (m, 2H), 4.07 – 4.02 (m, 1H), 2.24 – 2.01 (m, 3H), 1.96 – 1.77 (m, 3H), 1.37 (d, *J* = 6.2 Hz, 12H), 1.10 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 70.2 (d, *J* = 6.6 Hz), 59.8 (d, *J* = 18.8 Hz), 32.0, 31.9 (d, *J* = 4.0 Hz), 25.3 (d, *J* = 143.4 Hz), 24.0, 12.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.9.

FT-IR (film) 3458, 2977, 1715, 1645, 1455, 1386, 1242, 1107, 1012, 889, 805 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{11}H_{25}BrO_3P$: 315.0719, found: 315.0721.



Dibenzyl (3-bromobutyl)phosphonate. The title compound was synthesized according to **GP-1** from dibenzyl (3-hydroxybutyl)phosphonate (6.54 g, 19.6 mmol) and purified by flash column chromatography on silica gel (33% EtOAc/CH_2Cl_2). 3.75 g (9.4 mmol, 48% yield). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 10H), 5.09 (dd, *J* = 11.8, 8.9 Hz, 2H), 5.04 – 4.93 (m, 2H), 4.12 – 4.05 (m, 1H), 2.14 – 1.82 (m, 4H), 1.66 (d, *J* = 6.7 Hz, 3H).

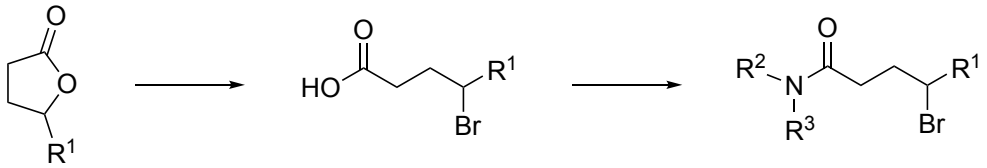
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.3 (d, *J* = 5.9 Hz), 128.7, 128.5, 128.0 (d, *J* = 2.5 Hz), 67.31 (d, *J* = 6.4 Hz), 67.28 (d, *J* = 6.4 Hz), 51.0 (d, *J* = 19.6 Hz), 33.7 (d, *J* = 3.9 Hz), 26.1, 24.6 (d, *J* = 141.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1.

FT-IR (film) 3467, 2958, 1638, 1497, 1456, 1380, 1250, 1027, 925, 856, 732, 699 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{18}H_{23}BrO_3P$: 397.0563, found: 397.0558.

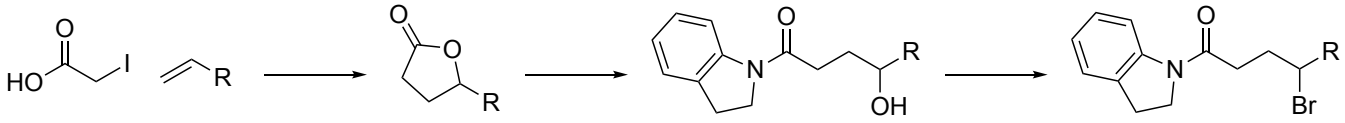
General Procedure 2 (GP-2) for the synthesis of γ-bromoamides.



The γ-bromoacids were synthesized following a literature procedure.[4]

In an oven-dried round-bottom flask, anhydrous CH_2Cl_2 ([γ-bromo acid] = 0.30 M) and oxalyl chloride (1.5 equiv) were added under nitrogen. The solution was cooled to 0 °C, and the γ-bromoacid (1.0 equiv) was added. Next, DMF (0.10 equiv) was added dropwise, and the reaction was monitored at 0 °C for 2 h, at which time gas evolution ended. The reaction mixture was concentrated to remove the excess oxalyl chloride and CH_2Cl_2, affording the corresponding 4-bromo acyl chloride, which was then dissolved in dry Et_2O (0.10 M) under a nitrogen atmosphere. The resulting solution was cooled to 0 °C, and the amine (1.0 equiv) was added slowly, followed by the addition of NEt_3 (2.0 equiv). The resulting suspension was allowed to warm to room temperature and stir for 1 h. The suspension was filtered to remove the triethylamine hydrochloride salt, which was washed twice with Et_2O. After removing Et_2O on a rotary evaporator, the residue was recrystallized from EtOAc/hexanes to afford the product as white solid.

General Procedure 3 (GP-3) for the synthesis of γ-bromoamides.

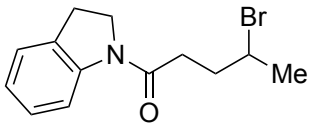


The γ-lactones were synthesized following a literature procedure.[5]

In accordance with a literature procedure,[6] triethylamine (1.5 equiv) was added dropwise to a suspension of $AlCl_3$ (1.1 equiv) in CH_2Cl_2 (0.20 M) at 0 °C (caution: exotherm). After the addition of triethylamine, the suspension was allowed to warm to room temperature. A solution of indoline (1.1 equiv) and γ-lactone (1.0 equiv) in CH_2Cl_2 (1.0 M) was added over 15 min, and the mixture stirred at room temperature for 12 h before quenching with a mixture of ice and water. The mixture was then further stirred for 30 min, and the resulting suspension was filtered through celite, and the organic phase was separated. The aqueous phase was extracted twice with CH_2Cl_2, and the organic phases were combined. After concentration of the

organic phase on a rotary evaporator, the residue was purified by flash column chromatography on silica gel to afford the γ-hydroxyamide.

Under a nitrogen atmosphere, a solution of PBr_3 (0.40 equiv) in CH_2Cl_2 (0.50 M) was added dropwise to the solution of γ-hydroxyamide (1.0 equiv, 0.20 M in CH_2Cl_2) and pyridine (0.40 equiv) at 0 °C. After the addition of PBr_3, the solution was allowed to warm to room temperature and stir for 16 h. The solution was then concentrated, and the residue was purified by flash chromatography through a short column of silica gel (height: 5 cm) with Et_2O as the eluent to afford the γ-bromoamide as white solid.



4-Bromo-1-(indolin-1-yl)pentan-1-one. The title compound was synthesized according to **GP-2** from 4-bromopentanoic acid (3.62 g, 20.0 mmol) and indoline (2.38 g, 20.0 mmol), and it was recrystallized from EtOAc/hexane. 4.84 g (17.2 mmol, 86% yield). White solid.

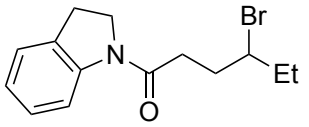
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 4.36 (dqd, *J* = 9.8, 6.6, 3.1 Hz, 1H), 4.26 – 4.05 (m, 2H), 3.28 (t, *J* = 8.5 Hz, 2H), 2.72 (td, *J* = 7.2, 6.5, 2.3 Hz, 2H), 2.40 (dtd, *J* = 15.0, 7.5, 3.1 Hz, 1H), 2.14 (ddt, *J* = 12.8, 10.0, 6.4 Hz, 1H), 1.85 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 142.9, 131.1, 127.6, 124.6, 123.7, 116.9, 51.9, 48.0, 35.7, 34.0, 28.0, 26.9.

FT-IR (film) 3438, 2918, 2478, 1769, 1667, 1598, 1485, 1416, 1292, 1262, 1174, 1118, 939, 760 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{13}H_{17}BrNO$: 282.0488, found: 282.0487.

m.p.: 92 °C.



4-Bromo-1-(indolin-1-yl)hexan-1-one. The title compound was synthesized according to **GP-2** from 4-bromohexanoic acid (6.31 g, 32.3 mmol) and indoline (3.85 g, 32.3 mmol), and it was recrystallized from EtOAc/hexane. 8.13 g (27.4 mmol, 85% yield). White solid.

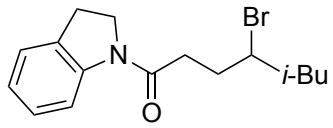
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.27 – 3.97 (m, 3H), 3.23 (t, *J* = 8.5 Hz, 2H), 2.78 – 2.58 (m, 2H), 2.40 (dtd, *J* = 15.1, 7.6, 2.8 Hz, 1H), 2.21 – 2.05 (m, 1H), 2.03 – 1.85 (m, 2H), 1.12 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 142.9, 131.1, 127.5, 124.6, 123.6, 116.9, 60.5, 47.9, 33.9, 33.5, 32.7, 28.0, 12.1.

FT-IR (film) 3422, 2965, 1662, 1482, 1412, 1284, 1115, 755 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{19}BrNO$: 296.0645, found: 296.0650.

m.p.: 95 °C.



4-Bromo-1-(indolin-1-yl)-6-methylheptan-1-one. The title compound was synthesized according to **GP-2** from 4-bromo-6-methylheptanoic acid (4.46 g, 20.0 mmol) and indoline (2.38 g, 20.0 mmol), and it was recrystallized from EtOAc/hexane. 3.44 g (10.6 mmol, 53% yield). White solid.

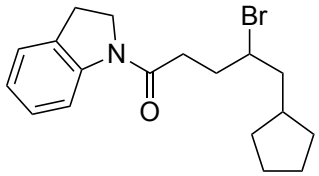
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.20 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 4.26 (td, *J* = 9.7, 4.1 Hz, 1H), 4.16 – 4.05 (m, 2H), 3.23 (t, *J* = 8.4 Hz, 2H), 2.76 – 2.66 (m, 2H), 2.41 (dtd, *J* = 15.1, 7.6, 2.7 Hz, 1H), 2.14 – 2.03 (m, 1H), 2.02 – 1.87 (m, 2H), 1.68 – 1.62 (m, 1H), 0.97 (dd, *J* = 23.3, 6.5 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 142.9, 131.1, 127.5, 124.6, 123.6, 116.9, 56.9, 48.6, 47.9, 34.0, 33.9, 28.0, 26.5, 22.8, 21.4.

FT-IR (film) 3421, 2957, 1654, 1595, 1483, 1459, 1407, 1276, 765 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{23}BrNO$: 324.0958, found: 324.0956.

m.p.: 96 °C.



4-Bromo-5-cyclopentyl-1-(indolin-1-yl)pentan-1-one. The title compound was synthesized according to **GP-2** from diethyl 4-bromo-5-cyclopentylpentanoic acid (1.87 g, 7.5 mmol) and indoline (0.89 g, 7.5 mmol), and it was recrystallized from EtOAc/hexane. 1.70 g (4.9 mmol, 65% yield). White solid.

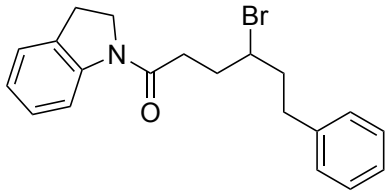
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.09 – 6.98 (m, 1H), 4.26 – 4.19 (m, 1H), 4.19 – 4.06 (m, 2H), 3.24 (t, *J* = 8.5 Hz, 2H), 2.84 – 2.61 (m, 2H), 2.47 – 2.40 (m, 1H), 2.19 – 2.01 (m, 3H), 1.89 – 1.79 (m, 3H), 1.69 – 1.62 (m, 2H), 1.61 – 1.52 (m, 2H), 1.25 – 1.01 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.2, 143.0, 131.1, 127.6, 124.6, 123.6, 116.9, 58.0, 48.0, 46.0, 38.4, 34.0, 33.9, 32.6, 32.0, 28.0, 25.1, 25.0.

FT-IR (film) 3400, 2948, 1655, 1599, 1482, 1411, 1289, 1118, 756 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{18}H_{25}BrNO$: 350.1114, found: 350.1110.

m.p.: 105 °C.



4-Bromo-1-(indolin-1-yl)-6-phenylhexan-1-one. The title compound was synthesized according to **GP-2** from 4-bromo-6-phenylhexanoic acid (2.79 g, 10.3 mmol) and indoline (10.3 mmol, 1.23 g), and it was recrystallized from EtOAc/hexane. 3.06 g (8.2 mmol, 80% yield). White solid.

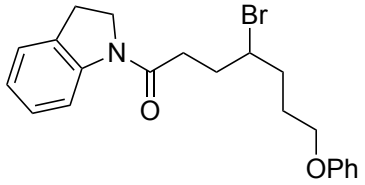
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.26 – 7.18 (m, 5H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 4.26 – 4.01 (m, 3H), 3.24 (t, *J* = 8.5 Hz, 2H), 2.96 (ddd, *J* = 14.3, 8.9, 5.8 Hz, 1H), 2.86 – 2.60 (m, 3H), 2.43 (dtd, *J* = 15.1, 7.6, 2.9 Hz, 1H), 2.34 – 2.05 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 142.9, 140.9, 131.1, 128.6, 128.5, 127.6, 126.1, 124.6, 123.7, 116.9, 57.6, 48.0, 41.3, 33.91, 33.87, 33.8, 28.0.

FT-IR (film) 3441, 2818, 2486, 1770, 1659, 1482, 1413, 1179, 1028, 752 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{20}H_{23}BrNO$: 372.0958, found: 372.0957.

m.p.: 85 °C.



4-Bromo-1-(indolin-1-yl)-7-phenoxyheptan-1-one. The title compound was synthesized according to **GP-3** from 4-hydroxy-1-(indolin-1-yl)-7-phenoxyheptan-1-one (2.59 g, 7.6 mmol) and purified by flash chromatography through a short column of silica gel (height: 5 cm) with Et_2O as the eluent. 1.36 g (3.4 mmol, 45% yield). White solid.

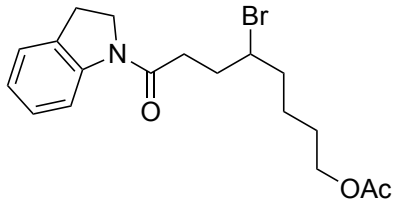
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.24 – 7.21 (m, 2H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 6.97 (tt, *J* = 7.4, 1.0 Hz, 1H), 6.94 – 6.88 (m, 2H), 4.30 – 4.22 (m, 1H), 4.19 – 4.07 (m, 2H), 4.04 – 4.02 (m, 2H), 3.24 (t, *J* = 8.5 Hz, 2H), 2.72 (t, *J* = 7.1 Hz, 2H), 2.45 (dtd, *J* = 15.0, 7.5, 2.9 Hz, 1H), 2.22 – 2.04 (m, 4H), 2.04 – 1.91 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 158.9, 142.9, 131.1, 129.5, 127.6, 124.6, 123.7, 120.7, 116.9, 114.5, 66.9, 58.0, 48.0, 36.3, 33.9, 33.8, 28.0, 27.6.

FT-IR (film) 3418, 2919, 2484, 1770, 1660, 1599, 1483, 1415, 1245, 1172, 1047, 755 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{21}H_{25}BrNO_2$: 402.1063, found: 402.1066.

m.p.: 98 °C.



5-Bromo-8-(indolin-1-yl)-8-oxooctyl acetate. The title compound was synthesized according to **GP-3** from 5-hydroxy-8-(indolin-1-yl)-8-oxooctyl acetate (3.07 g, 9.6 mmol) and purified by flash chromatography through a short column of silica gel (height: 5 cm) with Et_2O as the eluent. 1.30 g (3.4 mmol, 35% yield). White solid.

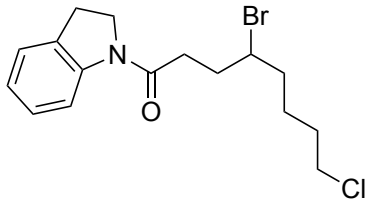
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 – 8.22 (m, 1H), 7.27 – 7.24 (m, 2H), 7.08 (td, *J* = 7.4, 1.1 Hz, 1H), 4.28 – 4.22 (m, 1H), 4.22 – 4.08 (m, 4H), 3.28 (t, *J* = 8.5 Hz, 2H), 2.75 (t, *J* = 6.9 Hz, 2H), 2.45 (dtd, *J* = 15.0, 7.5, 2.8 Hz, 1H), 2.18 – 2.10 (m, 4H), 2.01 – 1.97 (m, 2H), 1.79 – 1.68 (m, 3H), 1.64 – 1.57 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.2, 170.1, 142.9, 131.1, 127.6, 124.6, 123.7, 116.9, 64.2, 58.1, 47.9, 39.2, 33.9, 33.8, 28.04, 28.01, 24.2, 21.1.

FT-IR (film) 3456, 2948, 1735, 1659, 1598, 1412, 1364, 1242, 1044, 757 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{18}H_{25}BrNO_3$: 382.1012, found: 382.1009.

m.p.: 54 °C.



4-Bromo-8-chloro-1-(indolin-1-yl)octan-1-one. The title compound was synthesized according to **GP-2** from 4-bromo-8-chlorooctanoic acid (1.70 g, 6.6 mmol) and indoline (6.6 mmol, 0.79 g), and it was recrystallized from EtOAc/hexane. 1.18 g (3.3 mmol, 50% yield). White solid.

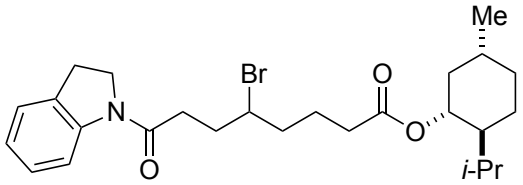
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.9 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.08 – 6.97 (m, 1H), 4.21 (dq, *J* = 10.3, 7.3, 5.0 Hz, 1H), 4.17 – 4.03 (m, 2H), 3.58 (t, *J* = 6.5 Hz, 2H), 3.24 (t, *J* = 8.5 Hz, 2H), 2.70 (t, *J* = 6.9 Hz, 2H), 2.41 (dtd, *J* = 15.0, 7.5, 2.8 Hz, 1H), 2.10 (ddt, *J* = 12.6, 10.3, 6.3 Hz, 1H), 1.98 – 1.92 (m, 2H), 1.90 – 1.75 (m, 3H), 1.69 – 1.62 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 142.9, 131.1, 127.6, 124.6, 123.7, 116.9, 57.9, 47.9, 44.7, 38.9, 33.8, 32.0, 28.0, 25.0.

FT-IR (film) 3477, 2942, 2731, 2615, 2485, 1770, 1660, 1482, 1416, 1291, 1181, 758 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{22}BrClNO$: 358.0568, found: 358.0566.

m.p.: 69 °C.



(*1R,2S,5R*)-2-Isopropyl-5-methylcyclohexyl 5-bromo-8-(indolin-1-yl)-8-oxooctanoate. The title compound was synthesized according to **GP-3** from (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 5-hydroxy-8-(indolin-1-yl)-8-oxooctanoate (2.89 g, 7.2 mmol) and purified by flash chromatography through a short column of silica gel (height: 5 cm) with Et_2O as the eluent. 1.61 g (3.3 mmol, 46% yield). White solid.

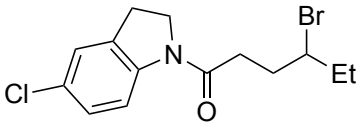
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.08 – 7.05 (m, 1H), 4.74 (td, *J* = 10.9, 4.4 Hz, 1H), 4.23 (dtd, *J* = 9.6, 6.0, 2.8 Hz, 1H), 4.19 – 4.06 (m, 2H), 3.26 (t, *J* = 8.5 Hz, 2H), 2.74 – 2.71 (m, 2H), 2.43 – 2.36 (m, 3H), 2.05 – 2.09 (m, 1H), 2.08 – 1.80 (m, 6H), 1.76 – 1.70 (m, 2H), 1.56 – 1.41 (m, 1H), 1.43 (ddt, *J* = 14.3, 11.2, 3.2 Hz, 1H), 1.18 – 0.86 (m, 9H), 0.81 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 170.0, 142.9, 131.1, 127.5, 124.6, 123.7, 116.9, 74.2, 65.9, 57.54, 57.52, 47.9, 47.0, 40.9, 38.82, 38.80, 34.2, 33.94, 33.91, 33.81, 33.79, 33.76, 31.4, 28.0, 26.3, 26.2, 23.38, 23.36, 23.19, 23.15, 22.1, 20.8, 16.32, 16.30, 15.3.

FT-IR (film) 2954, 1728, 1660, 1598, 1483, 1461, 1412, 1288, 1260, 1180, 983, 754 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{26}H_{39}BrNO_3$: 492.2108, found: 492.2105.

m.p.: 50 °C.



4-Bromo-1-(5-chloroindolin-1-yl)hexan-1-one. The title compound was synthesized according to **GP-2** from 4-bromohexanoic acid (1.95 g, 10.0 mmol) and 5-Cl-indoline (1.54 g, 10.0 mmol), and it was recrystallized from EtOAc/hexane. 2.72 g (8.2 mmol, 82% yield). White solid.

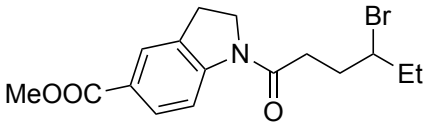
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.3 Hz, 1H), 7.17 – 7.16 (m, 2H), 4.22 – 4.01 (m, 3H), 3.21 (t, *J* = 8.5 Hz, 2H), 2.77 – 2.60 (m, 2H), 2.37 (dtd, *J* = 15.0, 7.6, 2.8 Hz, 1H), 2.17 – 2.04 (m, 1H), 2.02 – 1.85 (m, 2H), 1.10 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 141.7, 133.0, 128.5, 127.5, 124.7, 117.7, 60.2, 48.1, 33.8, 33.4, 32.7, 27.8, 12.2.

FT-IR (film) 3420, 2966, 1770, 1661, 1478, 1401, 1325, 1249, 1171, 1070, 826 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{18}BrClNO$: 330.0255, found: 330.0244.

m.p.: 65 °C.



Methyl 1-(4-bromohexanoyl)indoline-5-carboxylate. The title compound was synthesized according to **GP-2** from 4-bromohexanoic acid (1.10 g, 5.6 mmol) and methyl indoline-5-carboxylate (1.00 g, 5.6 mmol), and it was recrystallized from EtOAc/hexane. 1.32 g (3.7 mmol, 67% yield). White solid.

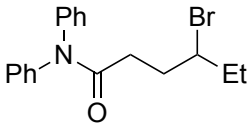
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.88 (s, 1H), 4.26 – 4.08 (m, 3H), 3.91 (s, 3H), 3.27 (t, *J* = 8.5 Hz, 2H), 2.87 – 2.63 (m, 2H), 2.39 (dtd, *J* = 15.0, 7.6, 2.8 Hz, 1H), 2.15 – 2.07 (m, 1H), 2.04 – 1.84 (m, 2H), 1.11 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 166.8, 146.9, 131.3, 130.2, 126.0, 125.3, 116.1, 60.1, 52.0, 48.4, 34.1, 33.3, 32.7, 27.6, 12.2.

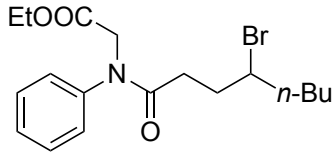
FT-IR (film) 2948, 1714, 1668, 1607, 1488, 1445, 1401, 1334, 1272, 1203, 1104, 768 cm^{-1}.

HRMS (LC-MS) *m*/*z* (M+H)$^+$ calcd for $C_{16}H_{21}BrNO_3$: 354.0699, found: 354.0695.

m.p.: 94 °C.



4-Bromo-*N*,*N*-diphenylhexanamide. The title compound was synthesized following a literature procedure; the characterization data are in accordance with the literature.[4]



Ethyl *N*-(4-bromooctanoyl)-*N*-phenylglycinate. The title compound was synthesized according to **GP-2** from 4-bromooctanoic acid (2.23 g, 10.0 mmol) and ethyl phenylglycinate (1.79 g, 10.0 mmol), and purified by flash column chromatography on silica gel (10% EtOAc/hexane). 2.37 g (6.2 mmol, 62% yield). Colorless oil.

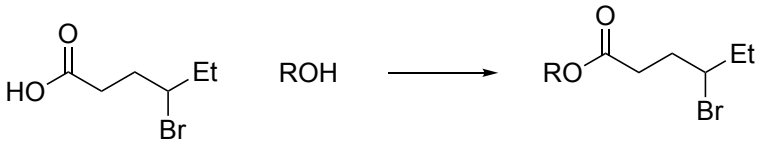
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.41 – 7.37 (m, 3H), 4.44 – 4.30 (m, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.03 (dtd, *J* = 10.2, 5.4, 2.8 Hz, 1H), 2.46 – 2.31 (m, 2H), 2.29 – 2.17 (m, 1H), 1.99 – 1.92 (m, 1H), 1.81 – 1.75 (m, 2H), 1.56 – 1.43 (m, 1H), 1.43 – 1.23 (m, 6H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 169.2, 142.6, 129.9, 128.4, 128.1, 61.3, 58.1, 51.4, 39.1, 34.4, 32.1, 29.7, 22.1, 14.2, 14.0.

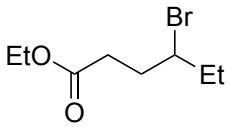
FT-IR (film) 3440, 2932, 1748, 1655, 1495, 1416, 1203, 1022, 703 cm^{-1}.

HRMS (LC-MS) *m*/*z* (M+H)$^+$ calcd for $C_{18}H_{27}BrNO_3$: 384.1169, found: 384.1165.

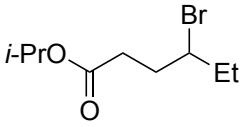
General Procedure 4 (GP-4) for the synthesis of γ-bromoesters.



To a solution of the γ-bromoacid (1.0 equiv) in CH_2Cl_2 (0.40 M) at 0 °C was added EDC·HCl (1.1 equiv) and DMAP (0.050 equiv). The resulting solution was stirred at 0 °C for 5 min, and then the alcohol (1.5 equiv) was added in one portion. The reaction mixture was allowed to warm to room temperature and stir for 12 h. Next, aqueous HCl (1 M; same volume as CH_2Cl_2) was added to quench the reaction, and the organic phase was separated. The aqueous phase was extracted three times with CH_2Cl_2, and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel to afford the desired γ-bromoester.



Ethyl 4-bromohexanoate. The title compound was synthesized following a literature procedure; the characterization data are in accordance with the literature.[7]



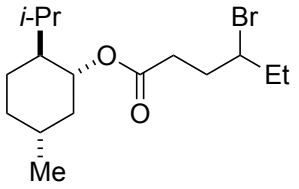
Isopropyl 4-bromohexanoate. The title compound was synthesized according to **GP-4** from 4-bromohexanoic acid (3.90 g, 20.0 mmol) and isopropanol (1.80 g, 30.0 mmol), and it was purified by flash column chromatography on silica gel (10% EtOAc/hexane). 2.95 g (12.4 mmol, 62% yield). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.07 (hept, *J* = 6.3 Hz, 1H), 4.10 – 4.02 (m, 1H), 2.62 (ddd, *J* = 16.5, 8.6, 5.6 Hz, 1H), 2.53 (ddd, *J* = 16.5, 8.6, 6.9 Hz, 1H), 2.27 – 2.20 (m, 1H), 2.16 – 2.04 (m, 1H), 2.01 – 1.83 (m, 2H), 1.30 (dd, *J* = 6.2, 1.7 Hz, 6H), 1.12 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 77.3, 59.1, 33.7, 32.8, 32.3, 21.9, 21.8, 12.1.

FT-IR (film) 2977, 1737, 1456, 1375, 1193, 1108, 974, 825 cm^{-1}.

LRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_9H_{18}BrO_2$: 237.1, found: 237.1.



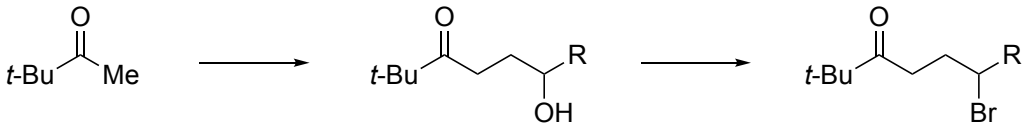
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-bromohexanoate. The title compound was synthesized according to **GP-4** from 4-bromohexanoic acid (3.90 g, 20.0 mmol) and (L)-menthol (4.69 g, 30.0 mmol), and it was purified by flash column chromatography on silica gel (10% EtOAc/hexane). 4.79 g (14.4 mmol, 72% yield). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.74 (td, *J* = 10.9, 4.4 Hz, 1H), 4.06 (dtd, *J* = 10.9, 8.9, 5.2 Hz, 1H), 2.68 – 2.49 (m, 2H), 2.28 – 2.20 (m, 1H), 2.16 – 2.07 (m, 1H), 2.07 – 2.01 (m, 1H), 1.97 – 1.88 (m, 3H), 1.77 – 1.71 (m, 2H), 1.57 – 1.51 (m, 1H), 1.43 (ddt, *J* = 14.1, 11.0, 3.1 Hz, 1H), 1.18 – 1.01 (m, 6H), 1.00 – 0.88 (m, 6H), 0.82 (dd, *J* = 7.0, 1.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 74.4, 59.13, 59.06, 46.99, 46.97, 40.93, 40.91, 34.2, 33.8, 33.7, 32.80, 32.75, 32.36, 32.35, 31.4, 26.29, 26.26, 23.40, 23.37, 22.1, 20.80, 20.78, 16.32, 16.30, 12.1.

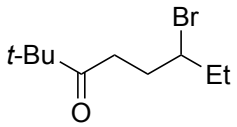
FT-IR (film) 2932, 1732, 1455, 1372, 1256, 1196, 1099, 1012, 983, 914, 844 cm^{-1}.

General Procedure 5 (GP-5) for the synthesis of γ-bromoketones.



In accordance with a literature procedure,[8] a solution of the ketone (2.0 equiv) in anhydrous toluene (2.0 M) was added over 10 min to a solution of LiHMDS in hexane (1.0 M; 2.4 equiv) at 0 °C. The mixture was stirred at 0 °C for 30 min, and then a solution of the epoxide (1.0 equiv) in anhydrous toluene (1.0 M) was added over 5 min. Next, $Y(OTf)_3$ (0.10 equiv) was added to the reaction mixture at 0 °C. The mixture was allowed to warm to room temperature and stir for 12 h. The reaction was then quenched through the addition of a saturated aqueous solution of NH_4Cl (half the volume of toluene), and the organic phase was separated. The aqueous phase was extracted three times with CH_2Cl_2, and the organic phases were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography on silica gel to afford the γ-hydroxyketone.

The γ-hydroxyketone was then converted to a γ-bromoketone following the bromination procedure described in **GP-1**.

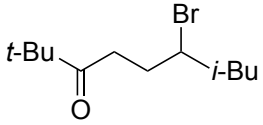


6-Bromo-2,2-dimethyloctan-3-one. The title compound was synthesized according to **GP-5** from 6-hydroxy-2,2-dimethyloctan-3-one (3.07 g, 17.8 mmol) and purified by flash column chromatography on silica gel (5% EtOAc/hexane). 3.34 g (14.2 mmol, 80% yield). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.02 – 3.97 (m, 1H), 2.84 – 2.71 (m, 2H), 2.19 (dtd, *J* = 14.9, 7.5, 3.1 Hz, 1H), 2.00 – 1.81 (m, 3H), 1.18 (s, 9H), 1.07 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.3, 60.2, 44.2, 34.7, 32.73, 32.70, 26.5, 12.2.

FT-IR (film) 2967, 1704, 1478, 1366, 1298, 1200, 1075, 1001, 842 cm^{-1}.

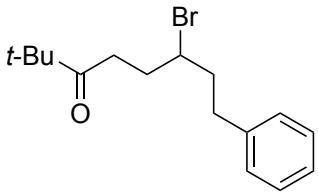


6-Bromo-2,2,8-trimethylnonan-3-one. The title compound was synthesized according to **GP-5** from 6-hydroxy-2,2,8-trimethylnonan-3-one (1.66 g, 8.3 mmol) and purified by flash column chromatography on silica gel (5% EtOAc/hexane). 1.55 g (5.9 mmol, 71% yield). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.14 (tdd, *J* = 9.6, 4.8, 3.1 Hz, 1H), 2.90 – 2.75 (m, 2H), 2.23 (dtd, *J* = 14.9, 7.5, 3.1 Hz, 1H), 2.02 – 1.84 (m, 3H), 1.66 – 1.57 (m, 1H), 1.22 (s, 9H), 1.00 (d, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.2, 56.6, 48.6, 44.2, 34.6, 33.3, 26.5, 26.4, 22.8, 21.4.

FT-IR (film) 2960, 1704, 1478, 1366, 1290, 1197, 1161, 1082, 992, 869 cm^{-1}.

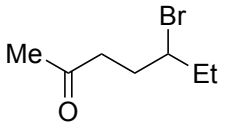


6-Bromo-2,2-dimethyl-8-phenyloctan-3-one. The title compound was synthesized according to **GP-5** from 6-hydroxy-2,2-dimethyl-8-phenyloctan-3-one (2.33 g, 9.4 mmol) and purified by flash column chromatography on silica gel (5% EtOAc/hexane). 1.95 g (6.3 mmol, 67% yield). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.25 – 7.21 (m, 2H), 4.05 – 3.97 (m, 1H), 2.93 (ddd, *J* = 14.2, 9.1, 5.3 Hz, 1H), 2.85 – 2.74 (m, 3H), 2.25 – 2.08 (m, 3H), 2.01 (ddt, *J* = 14.9, 9.9, 6.6 Hz, 1H), 1.18 (s, 9H).

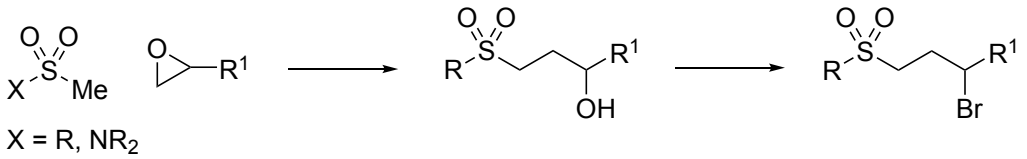
^{13}C NMR (126 MHz, $CDCl_3$) δ 215.1, 140.9, 128.53, 128.50, 126.1, 57.4, 44.2, 41.2, 34.7, 33.8, 33.2, 26.5.

FT-IR (film) 2964, 1703, 1603, 1455, 1366, 1226, 1072, 985, 749, 701 cm^{-1}.

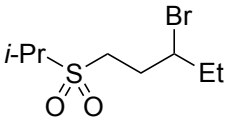


5-Bromoheptan-2-one. The title compound was synthesized following a literature procedure; the characterization data are in accordance with the literature.[9]

General Procedure 6 (GP-6) for the synthesis of γ-bromosulfones and γ-bromosulfonamides.



The γ-hydroxysulfones and γ-hydroxysulfonamides were synthesized following a literature procedure,[10] and they were then converted to the γ-bromosulfones and γ-bromosulfonamides following the bromination procedure described in **GP-1**.



3-Bromo-1-(isopropylsulfonyl)pentane. The title compound was synthesized according to **GP-6** from 1-(isopropylsulfonyl)pentan-3-ol (1.54 g, 7.9 mmol) and purified by flash column chromatography on silica gel (20% EtOAc/hexane). 1.76 g (6.8 mmol, 87% yield). White solid.

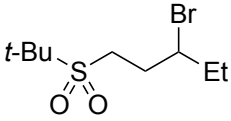
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.15 – 4.10 (m, 1H), 3.32 (ddd, *J* = 13.5, 10.3, 5.1 Hz, 1H), 3.23 – 3.08 (m, 2H), 2.49 (dddd, *J* = 14.8, 10.3, 5.4, 3.1 Hz, 1H), 2.31 (dtd, *J* = 14.9, 10.2, 5.1 Hz, 1H), 2.04 – 1.90 (m, 2H), 1.48 (d, *J* = 6.9 Hz, 6H), 1.14 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 57.3, 53.4, 47.6, 32.4, 30.3, 15.5, 15.2, 12.1.

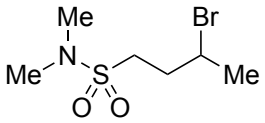
FT-IR (film) 3608, 2974, 1634, 1456, 1302, 1128, 1052, 954, 878, 802, 688 cm^{-1}.

LRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_8H_{18}BrO_2S$: 257.0, found: 257.0.

m.p.: 40 °C.



3-Bromo-1-(*tert*-butylsulfonyl)pentane. The title compound was synthesized following a literature procedure; the characterization data are in accordance with the literature.[4]



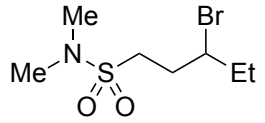
3-Bromo-*N,N*-dimethylbutane-1-sulfonamide. The title compound was synthesized according to **GP-6** from 3-hydroxy-*N,N*-dimethylbutane-1-sulfonamide (3.89 g, 21.5 mmol) and purified by flash column chromatography on silica gel (20% EtOAc/hexane). 4.94 g (20.2 mmol, 94% yield). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.25 (dqd, *J* = 10.1, 6.7, 3.5 Hz, 1H), 3.21 (ddd, *J* = 13.7, 9.8, 5.2 Hz, 1H), 3.07 (ddd, *J* = 13.7, 9.9, 5.7 Hz, 1H), 2.92 (s, 6H), 2.36 (dddd, *J* = 14.8, 9.7, 5.6, 3.5 Hz, 1H), 2.22 (dtd, *J* = 14.8, 9.8, 5.2 Hz, 1H), 1.78 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 48.9, 46.6, 37.5, 34.3, 26.4.

FT-IR (film) 3626, 2926, 1632, 1455, 1336, 1136, 962, 802, 749, 710 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_6H_{15}BrNO_2S$: 244.0001, found: 243.9998.



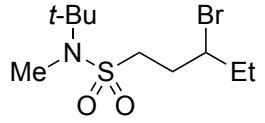
3-Bromo-*N,N*-dimethylpentane-1-sulfonamide. The title compound was synthesized according to **GP-6** from 3-hydroxy-*N,N*-dimethylpentane-1-sulfonamide (3.91 g, 20.0 mmol) and purified by flash column chromatography on silica gel (20% EtOAc/hexane). 4.88 g (18.9 mmol, 95% yield). Colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.14 – 4.09 (m, 1H), 3.28 (ddd, *J* = 13.7, 10.0, 5.1 Hz, 1H), 3.11 (ddd, *J* = 13.7, 10.1, 5.6 Hz, 1H), 2.95 (s, 6H), 2.46 – 2.39 (m, 1H), 2.28 (dtd, *J* = 14.9, 9.9, 5.1 Hz, 1H), 2.02 – 1.88 (m, 2H), 1.13 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 57.3, 46.5, 37.5, 32.3, 32.1, 12.1.

FT-IR (film) 3626, 2970, 1622, 1455, 1200, 1136, 1056, 966, 905, 784, 748, 711, 671 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_7H_{17}BrNO_2S$: 258.0158, found: 258.0154.



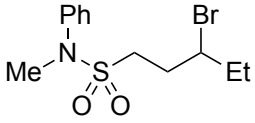
3-Bromo-*N*-(tert-butyl)-*N*-methylpentane-1-sulfonamide. The title compound was synthesized according to **GP-6** from *N*-(tert-butyl)-3-hydroxy-*N*-methylpentane-1-sulfonamide (2.95 g, 12.4 mmol) and purified by flash column chromatography on silica gel (20% EtOAc/hexane). 3.28 g (10.9 mmol, 88% yield). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 – 3.97 (m, 1H), 3.23 (ddd, *J* = 13.8, 9.9, 5.1 Hz, 1H), 3.08 (ddd, *J* = 13.8, 9.9, 5.6 Hz, 1H), 2.83 (s, 3H), 2.29 (dddd, *J* = 15.4, 9.8, 5.6, 3.3 Hz, 1H), 2.14 (dtd, *J* = 14.9, 9.8, 5.1 Hz, 1H), 1.87 – 1.77 (m, 2H), 1.38 (s, 9H), 1.00 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 58.6, 57.4, 53.2, 32.8, 32.38, 32.36, 29.4, 12.1.

FT-IR (film) 3626, 2976, 1456, 1367, 1317, 1268, 1128, 909, 816, 721, 662 cm^{-1}.

LRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{10}H_{23}BrNO_2S$: 300.1, found: 300.1.



3-Bromo-*N*-methyl-*N*-phenylpentane-1-sulfonamide. The title compound was synthesized according to **GP-6** from 3-hydroxy-*N*-methyl-*N*-phenylpentane-1-sulfonamide (2.55 g, 9.9 mmol) and purified by flash column chromatography on silica gel (20% EtOAc/hexane). 2.00 g (6.2 mmol, 63% yield). White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.42 (m, 4H), 7.34 – 7.32 (m, 1H), 4.02 (tdd, *J* = 8.8, 4.8, 2.8 Hz, 1H), 3.39 (s, 3H), 3.35 (ddd, *J* = 13.7, 10.0, 5.0 Hz, 1H), 3.16 (ddd, *J* = 13.7, 10.2, 5.5 Hz, 1H), 2.37 (dddd, *J* = 14.8, 10.1, 5.5, 3.2 Hz, 1H), 2.24 (ddt, *J* = 14.8, 9.8, 5.0 Hz, 1H), 1.91 – 1.84 (m, 2H), 1.06 (t, *J* = 7.3 Hz, 3H).

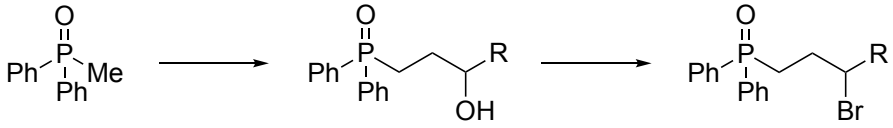
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 129.4, 127.5, 126.5, 57.1, 47.9, 38.5, 32.3, 32.2, 12.0.

FT-IR (film) 2972, 1596, 1493, 1344, 1143, 1067, 875, 767, 697 cm^{-1}.

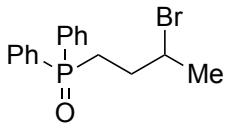
HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{12}H_{19}BrNO_2S$: 320.0314, found: 320.0320.

m.p.: 44 °C.

General Procedure 7 (GP-7) for the synthesis of γ-bromophosphine oxides.



The γ-hydroxyphosphine oxide was synthesized following a literature procedure.[11] The γ-hydroxyphosphine oxide was then converted to the γ-bromophosphine oxide following the bromination procedure described in **GP-3**.



(3-Bromobutyl)diphenylphosphine oxide. The title compound was synthesized according to **GP-7** from (3-hydroxybutyl)diphenylphosphine oxide (7.93 g, 28.9 mmol) and purified by flash column chromatography on silica gel (50% EtOAc/CH_2Cl_2). 2.00 g (13.0 mmol, 45% yield). White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 4H), 7.59 – 7.47 (m, 6H), 4.22 – 4.16 (m, 1H), 2.67 – 2.59 (m, 1H), 2.37 (dtd, *J* = 14.8, 12.3, 4.3 Hz, 1H), 2.21 (dtq, *J* = 15.8, 7.9, 4.0 Hz, 1H), 2.07 – 1.92 (m, 1H), 1.71 (d, *J* = 6.7 Hz, 2H).

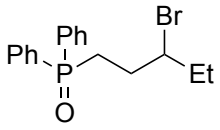
^{13}C NMR (101 MHz, $CDCl_3$) δ 133.0 (d, *J* = 99.2 Hz), 132.3 (d, *J* = 99.2 Hz), 131.93 (d, *J* = 2.5 Hz), 131.90 (d, *J* = 2.5 Hz), 130.8 (d, *J* = 15.5 Hz), 130.7 (d, *J* = 15.5 Hz), 128.80 (d, *J* = 11.7 Hz), 128.75 (d, *J* = 11.7 Hz), 52.1 (d, *J* = 16.5 Hz), 32.9 (d, *J* = 2.6 Hz), 28.3 (d, *J* = 72.2 Hz), 26.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 31.9.

FT-IR (film) 3419, 3057, 1635, 1437, 1178, 1121, 783, 750, 719, 696 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{19}BrOP$: 337.0351, found: 337.0360.

m.p.: 82 °C.



(3-Bromopentyl)diphenylphosphine oxide. The title compound was synthesized according to **GP-7** from (3-hydroxypentyl)diphenylphosphine oxide (4.04 g, 14.0 mmol) and purified by flash column chromatography on silica gel (20% EtOAc/hexane). 2.15 g (6.1 mmol, 44% yield). White solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 4H), 7.61 – 7.49 (m, 6H), 4.05 (dddd, *J* = 9.1, 7.1, 5.6, 3.3 Hz, 1H), 2.70 (dddd, *J* = 14.6, 11.8, 10.2, 4.4 Hz, 1H), 2.41 (dtd, *J* = 14.7, 12.3, 4.3 Hz, 1H), 2.28 (dddt, *J* = 15.4, 11.8, 7.7, 3.8 Hz, 1H), 2.13 – 2.00 (m, 1H), 1.91 – 1.86 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.0 (d, *J* = 99.0 Hz), 132.3 (d, *J* = 99.0 Hz), 131.93 (d, *J* = 2.8 Hz), 131.90 (d, *J* = 2.8 Hz), 130.8 (d, *J* = 17.1 Hz), 130.7 (d, *J* = 17.1 Hz), 128.80 (d, *J* = 11.7 Hz), 128.75 (d, *J* = 11.7 Hz), 60.7 (d, *J* = 15.9 Hz), 32.2, 30.7 (d, *J* = 2.5 Hz), 28.2 (d, *J* = 72.1 Hz), 12.2.

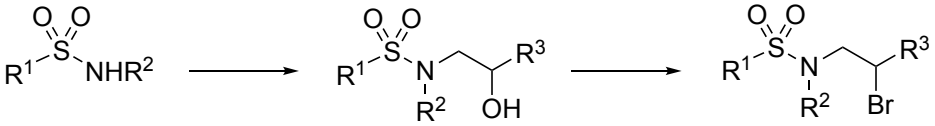
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.1.

FT-IR (film) 3419, 3057, 2967, 2934, 2363, 1646, 1437, 1182, 1120, 793, 751, 719, 696 cm^{-1}.

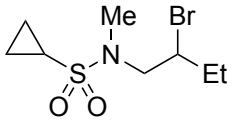
HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{21}BrOP$: 351.0508, found: 351.0516.

m.p.: 61 °C.

General Procedure 8 (GP-8) for the synthesis of sulfonyl-protected β-bromoamines.



The sulfonyl-protected β-hydroxyamine was synthesized following a literature procedure.[12] The sulfonyl-protected β-hydroxyamine was then converted to the sulfonyl-protected β-bromoamine following the bromination procedure described in **GP-1**.



***N*-(2-Bromobutyl)-*N*-methylcyclopropanesulfonamide.** The title compound was synthesized according to **GP-8** from *N*-(2-hydroxybutyl)-*N*-methylcyclopropanesulfonamide

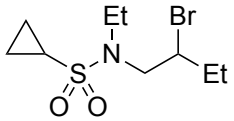
(3.11 g, 15.0 mmol) and purified by flash column chromatography on silica gel (20% Et_2O/hexane). 3.63 g (13.4 mmol, 90% yield). Colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ 4.18 – 4.13 (m, 1H), 3.67 (dd, *J* = 14.4, 7.3 Hz, 1H), 3.51 (dd, *J* = 14.4, 6.9 Hz, 1H), 3.04 (s, 3H), 2.41 (tt, *J* = 8.0, 4.9 Hz, 1H), 2.10 (dqd, *J* = 14.5, 7.3, 3.5 Hz, 1H), 1.85 – 1.76 (m, 1H), 1.27 – 1.24 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H), 1.09 – 1.04 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 56.9, 55.4, 36.7, 28.8, 27.2, 11.8, 4.68, 4.67.

FT-IR (film) 2970, 2362, 1156, 1337, 1192, 1149, 1042, 978, 927, 891, 756, 690 cm^{-1}.

LRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_8H_{17}BrNO_2S$: 270.0, found: 270.0.



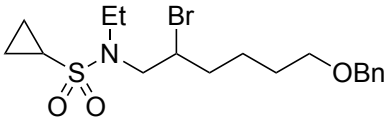
***N*-(2-Bromobutyl)-*N*-ethylcyclopropanesulfonamide.** The title compound was synthesized according to **GP-8** from *N*-ethyl-*N*-(2-hydroxybutyl)cyclopropanesulfonamide (6.64 g, 30.0 mmol) and purified by flash column chromatography on silica gel (20% Et_2O/hexane). 7.87 g (27.7 mmol, 92% yield). Colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ 4.22 – 4.16 (m, 1H), 3.62 (ddd, *J* = 54.2, 14.9, 7.1 Hz, 2H), 3.46 (ddt, *J* = 33.2, 14.8, 7.3 Hz, 2H), 2.42 (tt, *J* = 8.0, 4.9 Hz, 1H), 2.12 (dqd, *J* = 14.5, 7.3, 3.5 Hz, 1H), 1.78 (ddq, *J* = 14.5, 9.2, 7.2 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.26 (dd, *J* = 5.0, 2.0 Hz, 2H), 1.15 (t, *J* = 7.3 Hz, 3H), 1.07 – 1.05 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 56.1, 53.7, 43.9, 29.7, 28.9, 14.0, 12.0, 5.4, 5.3.

FT-IR (film) 2973, 1456, 1383, 1336, 1191, 1143, 1042, 890, 785, 743, 683 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_9H_{19}BrNO_2S$: 284.0314, found: 284.0312.



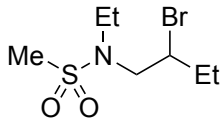
***N*-(6-(Benzyloxy)-2-bromohexyl)-*N*-methylcyclopropanesulfonamide.** The title compound was synthesized according to **GP-8** from *N*-(6-(benzyloxy)-2-hydroxyhexyl)-*N*-methylcyclopropanesulfonamide (3.71 g, 10.9 mmol) and purified by flash column chromatography on silica gel (20% Et_2O/hexane). 3.56 g (8.8 mmol, 81% yield). Colorless oil.

^1H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.36 (m, 4H), 7.32 – 7.29 (m, 1H), 4.53 (s, 2H), 4.23 – 4.18 (m, 1H), 3.68 – 3.35 (m, 6H), 2.41 – 2.36 (m, 1H), 2.07 – 2.01 (m, 1H), 1.83 – 1.63 (m, 4H), 1.60 – 1.54 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.23 – 1.19 (m, 2H), 1.08 – 0.99 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 128.4, 127.7, 127.5, 72.9, 67.0, 54.1, 53.9, 43.9, 35.4, 29.7, 29.1, 24.3, 14.0, 5.4, 5.3.

FT-IR (film) 2937, 1496, 1455, 1335, 1190, 1147, 1102, 1041, 890, 744, 698 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+Na)^+$ calcd for $C_{18}H_{29}BrNNaO_3S$: 440.0865, found: 440.0865.



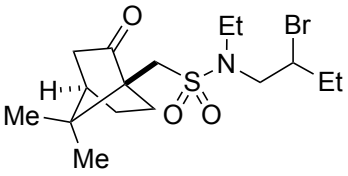
***N*-(2-Bromobutyl)-*N*-ethylmethanesulfonamide.** The title compound was synthesized according to **GP-8** from *N*-ethyl-*N*-(2-hydroxybutyl)methanesulfonamide (1.45 g, 7.4 mmol) and purified by flash column chromatography on silica gel (20% Et_2O/hexane). 1.35 g (5.2 mmol, 71% yield). Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 – 4.11 (m, 1H), 3.66 – 3.30 (m, 4H), 2.93 (s, 3H), 2.05 (dqd, *J* = 14.6, 7.3, 3.6 Hz, 1H), 1.74 (tdd, *J* = 14.6, 8.2, 4.5 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 55.9, 53.8, 43.9, 39.3, 28.9, 13.9, 11.9.

FT-IR (film) 3627, 2973, 1634, 1455, 1383, 1336, 1188, 1150, 1022, 965, 906, 774, 694 cm^{-1}.

LRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_7H_{17}BrNO_2S$: 258.0, found: 258.0.



***N*-(2-Bromobutyl)-1-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-ethylmethanesulfonamide.** The title compound was synthesized according to **GP-8** from 1-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-ethyl-*N*-(2-hydroxybutyl)methanesulfonamide (3.10 g, 9.4 mmol) and purified by flash column chromatography on silica gel (20% Et_2O/hexane). 2.47 g (6.3 mmol, 67% yield). Colorless oil.

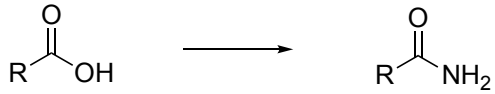
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.25 – 4.15 (m, 1H), 3.76 – 3.28 (m, 5H), 2.93 (dd, *J* = 34.1, 14.5 Hz, 1H), 2.55 (ddd, *J* = 14.8, 11.6, 4.0 Hz, 1H), 2.44 (dt, *J* = 18.4, 4.0 Hz, 1H), 2.19 – 2.05 (m, 3H), 2.00 (d, *J* = 18.4 Hz, 1H), 1.84 – 1.69 (m, 2H), 1.49 (ddd, *J* = 13.0, 9.3, 4.0 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 3H), 1.15 (td, *J* = 7.2, 2.7 Hz, 3H), 0.95 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 215.31, 215.28, 58.5, 56.2, 56.0, 54.1, 54.0, 48.4, 48.3, 47.9, 44.2, 44.0, 42.9, 42.6, 28.91, 28.88, 26.9, 25.33, 25.30, 20.1, 19.8, 14.49, 14.46, 12.03, 12.00.

FT-IR (film) 3467, 2966, 2322, 1747, 1455, 1417, 1337, 1201, 1148, 1050, 909, 778, 720 cm^{-1}.

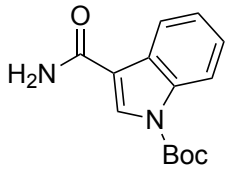
HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{29}BrNO_3S$: 394.1046, found: 394.1045.

General Procedure 9 (GP-9) for the synthesis of amides.

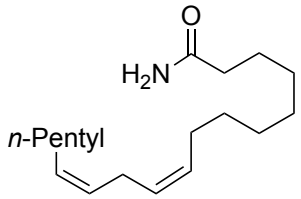


In accordance with a literature procedure,[13] Et_3N (3.0 equiv) and $ClCO_2Et$ (1.4 equiv) were added to a colorless solution of the acid (1.0 equiv; 0.050 M) in THF at 0 °C. After stirring for 30 min at 0 °C, an aqueous solution of NH_4Cl (1.5 equiv; 1.0 M) was added to the reaction mixture. The mixture was stirred at 0 °C for 30 min, and then H_2O (half of the volume of THF)

was added. The colorless clear solution was extracted with EtOAc, the aqueous phase was extracted with EtOAc, and the solvent was removed. The residue was purified by flash column chromatography on silica gel to afford the desired amide.



***tert*-Butyl 3-carbamoyl-1*H*-indole-1-carboxylate.** The title compound was synthesized following a literature procedure; the characterization data are in accordance with the literature.[14]



(9*Z*,12*Z*)-Octadeca-9,12-dienamide. The title compound was synthesized according to **GP-9** from (9*Z*,12*Z*)-octadeca-9,12-dienoic acid (2.81 g, 10.0 mmol) and purified by flash column chromatography on silica gel (EtOAc as eluent). 2.35 g (8.4 mmol, 84% yield). White solid.

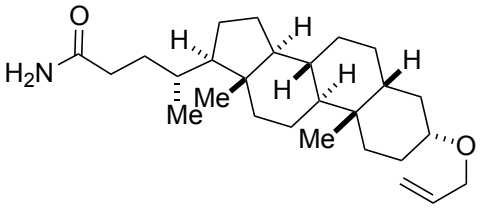
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.75 (brs, 1H), 5.52 (brs, 1H), 5.48 – 5.31 (m, 4H), 2.83 (t, *J* = 6.6 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 2.10 (q, *J* = 7.0 Hz, 4H), 1.69 (p, *J* = 7.6 Hz, 2H), 1.46 – 1.29 (m, 14H), 0.95 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 130.2, 130.0, 128.1, 127.9, 36.0, 31.5, 29.6, 29.4, 29.3, 29.2, 29.1, 27.21, 27.19, 25.6, 25.5, 22.6, 14.1.

FT-IR (film) 3356, 3008, 2927, 1660, 1468, 1410, 1216, 760 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{18}H_{34}NO$: 280.2635, found: 280.2631.

m.p.: 58 °C.



(*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-(Allyloxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanamide. The title compound was synthesized according to **GP-9** from (*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-(allyloxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoic acid (2.00 g, 4.8 mmol) and purified by flash column chromatography on silica gel (EtOAc as eluent). 1.85 g (4.5 mmol, 93% yield). White solid.

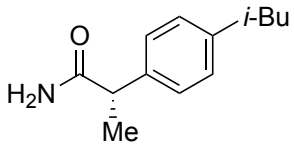
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 (ddt, *J* = 16.2, 10.7, 5.6 Hz, 1H), 5.76 (brs, 1H), 5.57 (brs, 1H), 5.32 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.19 (dt, *J* = 10.3, 1.6 Hz, 1H), 4.06 (dd, *J* = 5.6, 1.5 Hz, 2H), 3.35 (tt, *J* = 11.1, 4.5 Hz, 1H), 2.33 (ddd, *J* = 15.2, 10.7, 5.0 Hz, 1H), 2.16 (ddd, *J* = 14.8, 10.3, 6.1 Hz, 1H), 1.99 (dt, *J* = 12.4, 3.3 Hz, 1H), 1.95 – 1.75 (m, 6H), 1.66 – 1.58 (m, 2H), 1.53 – 1.23 (m, 11H), 1.20 – 1.06 (m, 5H), 1.03 – 0.86 (m, 7H), 0.69 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.3, 135.6, 116.5, 76.8, 69.0, 56.5, 55.9, 42.7, 42.1, 40.3, 40.2, 35.8, 35.44, 35.36, 34.9, 33.2, 32.8, 31.6, 28.3, 27.3, 27.2, 26.4, 24.2, 23.4, 20.8, 18.4, 12.1.

FT-IR (film) 3363, 3193, 2928, 2864, 1667, 1447, 1377, 1092, 919, 755 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{27}H_{46}NO_2$: 416.3523, found: 416.3524.

m.p.: 109 °C.



(*S*)-2-(4-Isobutylphenyl)propanamide. The title compound was synthesized according to **GP-9** from (*S*)-2-(4-isobutylphenyl)propanoic acid (2.00 g, 9.7 mmol) and purified by flash column chromatography on silica gel (EtOAc as eluent). 1.82 g (8.9 mmol, 91% yield). White solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 7.16 – 7.10 (m, 2H), 6.01 (brs, 1H), 5.43 (brs, 1H), 3.58 (q, *J* = 7.2 Hz, 1H), 2.47 (d, *J* = 7.2 Hz, 2H), 1.86 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.52 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 6H).

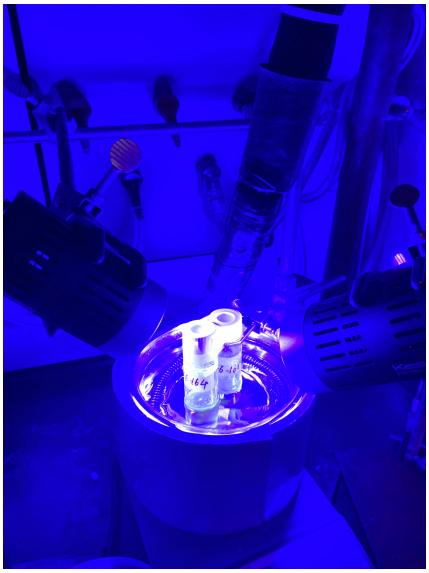
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 140.8, 138.5, 129.7, 127.3, 46.3, 45.0, 30.2, 22.4, 18.3.

FT-IR (film) 3343, 3189, 2950, 1637, 1406, 1276, 1112, 998, 761 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{13}H_{20}NO$: 206.1539, found: 206.1542.

m.p.: 126 °C.

IV. Enantioconvergent Substitutions

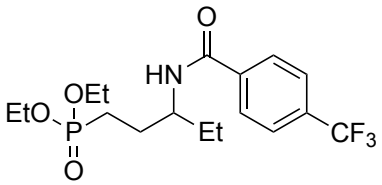


General Procedure 10 (GP-10): Coupling of amides with γ-bromophosphonates, γ-bromoketones, and sulfonyl-protected β-bromoamines. In the air, racemic bisphosphine ligand **P** (25.8 mg, 0.025 mmol, 5.0 mol%), chiral diamine ligand **N1*** (28.2 mg, 0.075 mmol, 15 mol%), and the amide (0.50 mmol) were weighed into an oven-dried 40 mL vial. The vial was sealed with a septum cap and was evacuated and backfilled with nitrogen (one cycle). The septum cap was removed, and $Cu(CH_3CN)_4PF_6$ (22.4 mg, 0.060 mmol, 12 mol%), $CsOPh{\cdot}H_2O$ (183 mg, 0.75 mmol, 1.5 equiv), and Cs_2CO_3 (244 mg, 0.75 mmol, 1.5 equiv) were rapidly weighed into the vial ($Cu(CH_3CN)_4PF_6$ is air-sensitive, whereas $CsOPh{\cdot}H_2O$ and Cs_2CO_3 are hygroscopic; it is recommended that they be stored and weighed in a glovebox, then transferred out of the glovebox), followed by the addition of an oven-dried cross-shaped stir bar. The vial was sealed with a septum cap that was then wrapped with electrical tape. The vial was then evacuated and backfilled with nitrogen (three cycles), and a nitrogen balloon was attached. Anhydrous *i*-Pr_2O (15 mL) was added via syringe, and the reaction mixture was allowed to stir at room temperature for 40 min. Next, the electrophile (0.60 mmol, 1.2 equiv) was added via syringe [If the electrophile was a solid, the electrophile was dissolved in *i*-Pr_2O (1.0 mL) and added as solution.]. The vial was then placed into a cryocool with a well-stirred isopropanol bath precooled to −5 °C. The reaction mixture was stirred at −5 °C for 5 min and the nitrogen balloon was removed. Vacuum grease was liberally applied to cover the punctures in the septum cap, and the reaction was irradiated with two PR 440 nm Kessil blue LED lamps, placed ~5 cm away, at −5 °C for 24 h, with efficient stirring. After the reaction was complete, the reaction mixture was transferred to a 250 mL round-bottom flask with the aid of MeOH. The mixture was concentrated, and the product was purified by flash column chromatography on silica gel.

General Procedure 11 (GP-11): Coupling of amides with γ-bromoamides. The procedure is the same as **GP-10**, except: **N2*** (18.0 mg, 0.075 mmol, 15 mol%) as the ligand, no Cs_2CO_3, 2-Me-THF as the solvent.

General Procedure 12 (GP-12): Coupling of amides with γ-bromoesters. The procedure is the same as **GP-10**, except: **N2*** (18.0 mg, 0.075 mmol, 15 mol%) as the ligand, –10 °C.

General Procedure 13 (GP-13): Coupling of amides with γ-bromosulfones, γ-bromosulfonamides, and γ-bromophosphine oxides. The procedure is the same as **GP-10**, except: electrophile (1.5 equiv), $Cu(CH_3CN)_4PF_6$ (28.0 mg, 0.075 mmol, 15 mol%), **N1*** (37.6 mg, 0.10 mmol, 20 mol%), $K_3PO_4 \cdot H_2O$ (173 mg, 0.75 mmol, 1.5 equiv) instead of Cs_2CO_3 as additive, 10 °C.



Diethyl (3-(4-(trifluoromethyl)benzamido)pentyl)phosphonate (Figure 2, entry 1). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S*,*S*)-**N1***: 183 mg, 93% yield, 93% ee; (*R*,*R*)-**N1***: 189 mg, 96% yield, 92% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 3.5 min (major), 4.9 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) 7.93 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 1H), 4.09 – 3.97 (m, 3H), 3.96 – 3.87 (m, 2H), 1.97 – 1.84 (m, 2H), 1.84 – 1.69 (m, 2H), 1.62 – 1.52 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 137.9, 133.0 (q, *J* = 32.6 Hz), 127.6, 125.5 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.4 Hz), 61.8 (d, *J* = 6.6 Hz), 51.4 (d, *J* = 12.8 Hz), 27.6, 26.7 (d, *J* = 4.5 Hz), 21.8 (d, *J* = 141.6 Hz), 16.4 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 6.0 Hz), 10.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3436, 3281, 2967, 1645, 1554, 1447, 1327, 1237, 1168, 1066, 968, 860, 680 cm^{-1}.

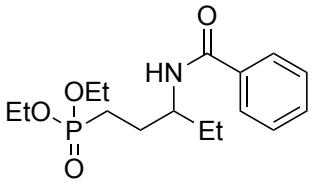
HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{26}F_3NO_4P$: 396.1546, found: 396.1547.

$[\alpha]^{24}_D$ = +0.6 (*c* 1.0, $CHCl_3$); 93% ee from (*S*,*S*)-**N1***.

Gram-scale reaction: Procedure **GP-10** was followed, except: instead of using a 40 mL vial, the reaction was conducted in a 100 mL round-bottom flask, with good stirring ensured. The

reaction was conducted with diethyl (3-bromopentyl)phosphonate (1.03 g, 3.6 mmol, 1.2 equiv) and 4-(trifluoromethyl)benzamide (567 mg, 3.0 mmol, 1.0 equiv).

(*S,S*)-**N1***: 1.03 g, 87% yield, 92% ee; (*R,R*)-**N1***: 0.98 g, 82% yield, 92% ee.



Diethyl (3-benzamidopentyl)phosphonate (Figure 2, entry 2). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and benzamide (77.8 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S,S*)-**N1***: 145 mg, 88% yield, 93% ee; (*R,R*)-**N1***: 147 mg, 90% yield, 92% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 5.8 min (major), 7.4 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.76 (m, 2H), 7.44 – 7.32 (m, 3H), 6.58 (d, *J* = 9.0 Hz, 1H), 4.10 – 3.90 (m, 5H), 1.92 – 1.83 (m, 1H), 1.81 – 1.66 (m, 3H), 1.64 – 1.43 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

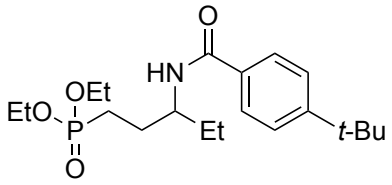
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 134.6, 131.4, 128.5, 127.0, 61.7 (d, *J* = 6.6 Hz), 51.3 (d, *J* = 15.1 Hz), 27.8, 27.3 (d, *J* = 4.5 Hz), 22.1 (d, *J* = 141.7 Hz), 16.4 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 6.1 Hz), 10.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.6.

FT-IR (film) 3437, 3318, 2931, 1641, 1544, 1310, 1238, 1023, 968, 826, 710 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{27}NO_4P$: 328.1672, found: 328.1667.

$[\alpha]^{24}_D$ = +0.6 (*c* 1.0, $CHCl_3$); 93% ee from (*S,S*)-**N1***.



Diethyl (3-(4-(*tert*-butyl)benzamido)pentyl)phosphonate (Figure 2, entry 3). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and 4-(*tert*-butyl)benzamide (88.6 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (EtOAc→3% MeOH/EtOAc). Colorless oil.

(*S,S*)-**N1***: 183 mg, 96% yield, 89% ee; (*R,R*)-**N1***: 190 mg, 99% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (30% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.8 min (major), 4.0 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 2H), 7.40 – 7.35 (m, 2H), 6.35 (d, *J* = 9.0 Hz, 1H), 4.10 – 3.89 (m, 5H), 1.92 – 1.83 (m, 1H), 1.81 – 1.64 (m, 3H), 1.62 – 1.45 (m, 2H), 1.26 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

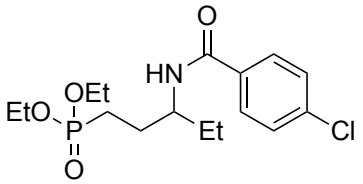
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 154.9, 131.7, 126.8, 125.5, 61.7 (d, *J* = 6.6 Hz), 51.2 (d, *J* = 15.3 Hz), 34.9, 31.2, 28.0, 27.3 (d, *J* = 4.5 Hz), 22.1 (d, *J* = 141.7 Hz), 16.4 (d, *J* = 6.2 Hz), 16.3 (d, *J* = 6.2 Hz), 10.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.6.

FT-IR (film) 3417, 2918, 2133, 1932, 1643, 1518, 1017, 848, 680 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{20}H_{35}NO_4P$: 384.2298, found: 384.2298.

$[\alpha]^{24}_D$ = –5.8 (*c* 1.0, $CHCl_3$); 89% ee from (*S*,*S*)-**N1***.



Diethyl (3-(4-chlorobenzamido)pentyl)phosphonate (Figure 2, entry 4). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and 4-chlorobenzamide (77.8 mg, 0.50 mmol). The product was purified by flash column chromatography (EtOAc→3% MeOH/EtOAc). Colorless oil.

(*S*,*S*)-**N1***: 172 mg, 95% yield, 92% ee; (*R*,*R*)-**N1***: 177 mg, 98% yield, 92% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 2.6 min (major), 3.4 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 2H), 7.43 – 7.35 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 1H), 4.15 – 4.04 (m, 3H), 4.04 – 3.96 (m, 2H), 2.01 – 1.73 (m, 4H), 1.69 – 1.55 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H).

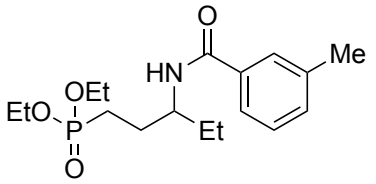
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 137.5, 133.0, 129.0, 128.6, 61.8 (d, *J* = 6.6 Hz), 51.3 (d, *J* = 13.4 Hz), 27.6, 26.9 (d, *J* = 4.6 Hz), 21.9 (d, *J* = 141.6 Hz), 16.4 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 6.0 Hz), 10.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8.

FT-IR (film) 3425, 3288, 2966, 1642, 1547, 1487, 1316, 1234, 1092, 1016, 967, 790 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{26}ClNO_4P$: 362.1282, found: 362.1282.

$[\alpha]^{24}_D$ = +0.5 (*c* 1.0, $CHCl_3$); 92% ee from (*S*,*S*)-**N1***.



Diethyl (3-(3-methylbenzamido)pentyl)phosphonate (Figure 2, entry 5). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and 3-methylbenzamide (67.6 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S*,*S*)-**N1***: 155 mg, 91% yield, 94% ee; (*R*,*R*)-**N1***: 146 mg, 86% yield, 92% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 5.6 min (major), 7.2 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 1H), 7.54 – 7.51 (m, 1H), 7.24 – 7.21 (m, 2H), 6.42 (d, *J* = 9.0 Hz, 1H), 4.08 – 3.89 (m, 5H), 2.32 (s, 3H), 1.91 – 1.82 (m, 1H), 1.81 – 1.65 (m, 3H), 1.62 – 1.44 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

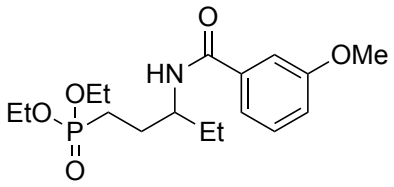
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 138.3, 134.6, 132.1, 128.4, 127.8, 123.9, 61.7 (d, *J* = 6.6 Hz), 51.3 (d, *J* = 15.9 Hz), 27.9, 27.4 (d, *J* = 4.5 Hz), 22.2 (d, *J* = 141.8 Hz), 21.3, 16.5 (d, *J* = 6.4 Hz), 16.4 (d, *J* = 6.4 Hz), 10.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5.

FT-IR (film) 3444, 2918, 2123, 1643, 1537, 1306, 1170, 1020, 971, 822, 725 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{29}NO_4P$: 342.1829, found: 342.1828.

$[\alpha]^{24}_D$ = +0.6 (*c* 1.0, $CHCl_3$); 94% ee from (*S*,*S*)-**N1***.



Diethyl (3-(3-methoxybenzamido)pentyl)phosphonate (Figure 2, entry 6). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and 3-methoxybenzamide (75.6 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S*,*S*)-**N1***: 141 mg, 79% yield, 89% ee; (*R*,*R*)-**N1***: 149 mg, 83% yield, 89% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 8.5 min (minor), 10.7 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 2.4, 1.6 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.03 (ddd, *J* = 7.8, 2.6, 1.4 Hz, 1H), 6.57 (d, *J* = 8.9 Hz, 1H), 4.18 – 3.98 (m, 5H), 3.86 (s, 3H), 2.01 – 1.91 (m, 1H), 1.89 – 1.73 (m, 3H), 1.71 – 1.52 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H).

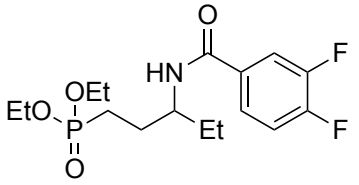
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 159.8, 136.1, 129.5, 118.7, 117.7, 112.4, 61.7 (d, *J* = 5.6 Hz), 55.4, 51.4 (d, *J* = 15.2 Hz), 27.9, 27.2 (d, *J* = 4.5 Hz), 22.1 (d, *J* = 141.8 Hz), 16.5 (d, *J* = 6.5 Hz), 16.4 (d, *J* = 6.5 Hz), 10.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.6.

FT-IR (film) 3306, 2933, 2098, 1634, 1254, 1032, 973, 832 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{29}NO_5P$: 358.1778, found: 358.1779.

$[\alpha]^{24}_D$ = +4.5 (*c* 1.0, $CHCl_3$); 89% ee from (*S*,*S*)-**N1***.



Diethyl (3-(3,4-difluorobenzamido)pentyl)phosphonate (Figure 2, entry 7). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and 3,4-difluorobenzamide (78.6 mg, 0.50 mmol). The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S*,*S*)-**N1***: 161 mg, 89% yield, 92% ee; (*R*,*R*)-**N1***: 168 mg, 92% yield, 91% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 3.4 min (major), 4.3 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (ddd, *J* = 11.0, 7.6, 2.2 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 7.19 (ddd, *J* = 9.8, 8.5, 7.9 Hz, 1H), 4.15 – 3.96 (m, 5H), 2.00 – 1.74 (m, 4H), 1.62 (pd, *J* = 7.3, 1.9 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1 (d, *J* = 1.5 Hz), 153.6 (d, *J* = 12.8 Hz), 151.2 (dd, *J* = 27.3, 12.8 Hz), 148.9 (d, *J* = 12.9 Hz), 131.6 (dd, *J* = 4.7, 3.8 Hz), 123.8 (dd, *J* = 7.0, 3.6 Hz), 117.1 (t, *J* = 18.3 Hz), 61.81 (d, *J* = 6.6 Hz), 61.79 (d, *J* = 6.6 Hz), 51.4 (d, *J* = 13.7 Hz), 27.5, 26.7 (d, *J* = 4.4 Hz), 21.8 (d, *J* = 141.6 Hz), 16.4 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 6.1 Hz), 10.4.

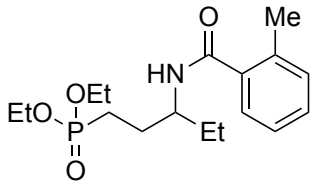
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ –133.3 (d, *J* = 20.9 Hz), –136.6 (d, *J* = 21.0 Hz).

FT-IR (film) 3321, 2928, 2052, 1642, 1286, 1027, 812, 681 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{25}F_2NO_4P$: 364.1484, found: 364.1483.

$[\alpha]^{24}_D$ = +0.6 (*c* 1.0, $CHCl_3$); 92% ee from (*S*,*S*)-**N1***.



Diethyl (3-(2-methylbenzamido)pentyl)phosphonate (Figure 2, entry 8). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate

(172 mg, 0.60 mmol) and 2-methylbenzamide (67.6 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S,S*)-**N1***: 128 mg, 75% yield, 90% ee; (*R,R*)-**N1***: 131 mg, 76% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK OD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.9 min (minor), 4.3 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 2H), 7.16 – 7.10 (m, 2H), 5.74 (d, *J* = 9.2 Hz, 1H), 4.07 – 3.93 (m, 5H), 2.37 (s, 3H), 1.92 – 1.52 (m, 5H), 1.50 – 1.39 (m, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H).

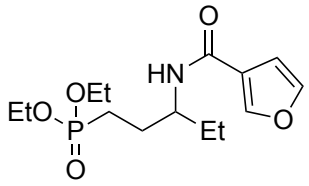
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 136.7, 135.9, 131.0, 129.8, 126.5, 125.7, 61.7 (d, *J* = 6.5 Hz), 61.6 (d, *J* = 6.5 Hz), 51.3 (d, *J* = 17.2 Hz), 28.0, 27.6 (d, *J* = 4.5 Hz), 22.4 (d, *J* = 142.2 Hz), 19.8, 16.5 (d, *J* = 6.0 Hz), 16.4 (d, *J* = 6.0 Hz), 10.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0.

FT-IR (film) 3466, 3304, 2930, 1642, 1536, 1230, 1024, 822, 738 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{29}NO_4P$: 342.1829, found: 342.1828.

$[\alpha]^{24}_D$ = +3.1 (*c* 1.0, $CHCl_3$); 90% ee from (*R,R*)-**N1***.



Diethyl (3-(furan-3-carboxamido)pentyl)phosphonate (Figure 2, entry 9). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and furan-3-carboxamide (55.6 mg, 0.50 mmol). The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S,S*)-**N1***: 116 mg, 73% yield, 90% ee; (*R,R*)-**N1***: 124 mg, 78% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 4.0 min (major), 4.8 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 1.5, 0.9 Hz, 1H), 7.42 (t, *J* = 2.0 Hz, 1H), 6.77 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.72 (d, *J* = 8.9 Hz, 1H), 4.17 – 3.98 (m, 5H), 1.97 – 1.72 (m, 4H), 1.67 – 1.49 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

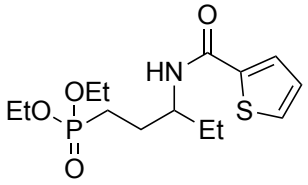
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 145.0, 143.5, 122.8, 108.6, 61.8 (t, *J* = 6.6 Hz), 50.6 (d, *J* = 12.9 Hz), 27.7, 26.8 (d, *J* = 4.5 Hz), 21.8 (d, *J* = 141.5 Hz), 16.4 (dd, *J* = 8.1, 6.1 Hz), 10.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 33.0.

FT-IR (film) 3468, 2918, 2174, 1643, 1229, 1016, 853, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{25}NO_5P$: 318.1465, found: 318.1461.

$[\alpha]^{24}_D$ = +3.8 (*c* 1.0, $CHCl_3$); 90% ee from (*S,S*)-**N1***.



Diethyl (3-(thiophene-2-carboxamido)pentyl)phosphonate (Figure 2, entry 10). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and thiophene-2-carboxamide (63.6 mg, 0.50 mmol). The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S,S*)-**N1***: 158 mg, 95% yield, 90% ee; (*R,R*)-**N1***: 161 mg, 96% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 7.0 min (major), 7.4 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.47 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.07 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.74 (d, *J* = 8.9 Hz, 1H), 4.18 – 3.97 (m, 5H), 2.07 – 1.90 (m, 1H), 1.90 – 1.74 (m, 3H), 1.70 – 1.53 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H).

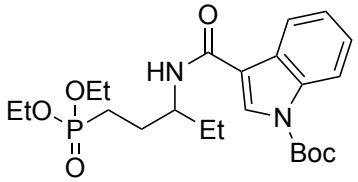
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 139.5, 129.9, 127.9, 127.6, 61.8 (d, *J* = 6.6 Hz), 61.7 (d, *J* = 6.6 Hz), 51.3 (d, *J* = 13.7 Hz), 27.8, 27.0 (d, *J* = 4.5 Hz), 21.9 (d, *J* = 141.6 Hz), 16.4 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 6.1 Hz), 10.4.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8.

FT-IR (film) 3437, 2917, 2153, 1632, 1538, 1304, 1017, 850 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{25}NO_4PS$: 334.1236, found: 334.1231.

$[\alpha]^{24}_D$ = +0.6 (*c* 1.0, $CHCl_3$); 90% ee from (*S,S*)-**N1***.



***tert*-Butyl 3-((1-(diethoxyphosphoryl)pentan-3-yl)carbamoyl)-1*H*-indole-1-carboxylate (Figure 2, entry 11).** The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and *tert*-butyl 3-carbamoyl-1*H*-indole-1-carboxylate (130 mg, 0.50 mmol). The product was purified by flash column chromatography (EtOAc→3% MeOH/EtOAc). Colorless oil.

(*S,S*)-**N1***: 194 mg, 83% yield, 90% ee; (*R,R*)-**N1***: 205 mg, 88% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.3 min (minor), 4.7 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.09 (m, 2H), 8.04 – 7.98 (m, 1H), 7.32 – 7.22 (m, 2H), 6.26 (d, *J* = 9.0 Hz, 1H), 4.15 – 3.92 (m, 5H), 1.95 – 1.85 (m, 1H), 1.85 – 1.67 (m, 3H), 1.61 (s, 9H), 1.59 – 1.48 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H).

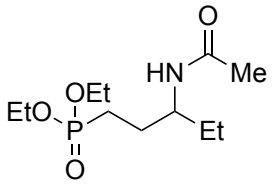
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 149.2, 135.6, 127.6, 125.1, 123.7, 121.1, 116.1, 115.3, 84.8, 61.72 (d, *J* = 6.5 Hz), 61.68 (d, *J* = 6.5 Hz), 50.9 (d, *J* = 15.3 Hz), 28.1, 28.0, 22.2 (d, *J* = 141.8 Hz), 16.4 (d, *J* = 5.9 Hz), 16.3 (d, *J* = 5.9 Hz), 10.5.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.6.

FT-IR (film) 3289, 2980, 1738, 1634, 1538, 1454, 1372, 1156, 1032, 966, 754, 665 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{23}H_{36}N_2O_6P$: 467.2305, found: 467.2300.

$[\alpha]^{24}_D$ = –3.4 (*c* 1.0, $CHCl_3$); 90% ee from (*S*,*S*)-**N1***.



Diethyl (3-acetamidopentyl)phosphonate (Figure 2, entry 12). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (241 mg, 0.84 mmol) and acetamide (41.4 mg, 0.70 mmol) at –20 °C. The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S*,*S*)-**N1***: 114 mg, 62% yield, 91% ee; (*R*,*R*)-**N1***: 114 mg, 62% yield, 91% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 6.1 min (major), 7.0 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 (d, *J* = 8.9 Hz, 1H), 4.18 – 4.06 (m, 4H), 3.93 – 3.86 (m, 1H), 2.03 (s, 3H), 1.93 – 1.76 (m, 3H), 1.71 – 1.62 (m, 1H), 1.61 – 1.53 (m, 1H), 1.52 – 1.44 (m, 1H), 1.364 (t, *J* = 7.0 Hz, 3H), 1.358 (t, *J* = 7.0 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H).

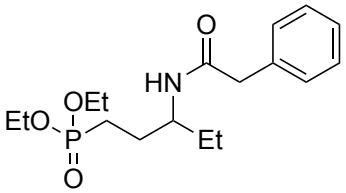
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 61.72 (d, *J* = 6.6 Hz), 61.68 (d, *J* = 6.6 Hz), 50.9 (d, *J* = 16.3 Hz), 27.8, 27.2 (d, *J* = 4.5 Hz), 23.4, 22.1 (d, *J* = 141.9 Hz), 16.4 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 6.0 Hz), 10.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5.

FT-IR (film) 3443, 3276, 2968, 1651, 1556, 1446, 1373, 1306, 1237, 1053, 969, 791 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{11}H_{25}NO_4P$: 266.1516, found: 266.1520.

$[\alpha]^{24}_D$ = +7.2 (*c* 1.0, $CHCl_3$); 91% ee from (*S*,*S*)-**N1***.



Diethyl (3-(2-phenylacetamido)pentyl)phosphonate (Figure 2, entry 13). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and 2-phenylacetamide (67.6 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S*,*S*)-**N1***: 134 mg, 79% yield, 90% ee; (*R*,*R*)-**N1***: 121 mg, 71% yield, 91% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 6.7 min (minor), 7.7 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 5H), 5.54 (d, *J* = 9.0 Hz, 1H), 4.14 – 4.04 (m, 4H), 3.93 – 3.86 (m, 1H), 3.61 (s, 2H), 1.83 – 1.79 (m, 1H), 1.76 – 1.66 (m, 2H), 1.64 – 1.48 (m, 2H), 1.39 – 1.30 (m, 7H), 0.86 (t, *J* = 7.4 Hz, 3H).

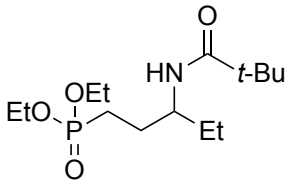
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 135.2, 129.3, 129.0, 127.3, 61.6 (d, *J* = 6.5 Hz), 61.5 (d, *J* = 6.5 Hz), 51.0 (d, *J* = 17.3 Hz), 44.0, 27.7, 27.3 (d, *J* = 4.5 Hz), 22.1 (d, *J* = 141.9 Hz), 16.4 (d, *J* = 6.0 Hz), 10.1.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2.

FT-IR (film) 3443, 3291, 3063, 2971, 1650, 1550, 1454, 1236, 1025, 970, 828, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{29}NO_4P$: 342.1829, found: 342.1827.

$[\alpha]^{24}_D$ = +1.7 (*c* 1.0, $CHCl_3$); 90% ee from (*S*,*S*)-**N1***.



Diethyl (3-pivalamidopentyl)phosphonate (Figure 2, entry 14). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and pivalamide (50.6 mg, 0.50 mmol) at –20 °C. The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S*,*S*)-**N1***: 111 mg, 72% yield, 90% ee; (*R*,*R*)-**N1***: 106 mg, 69% yield, 91% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 3.3 min (minor), 3.5 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.63 (d, *J* = 8.7 Hz, 1H), 4.21 – 4.04 (m, 4H), 3.92 (ddq, *J* = 13.4, 9.1, 5.1 Hz, 1H), 1.91 – 1.85 (m, 1H), 1.82 – 1.73 (m, 2H), 1.73 – 1.64 (m, 1H), 1.64 – 1.55 (m, 1H), 1.46 (dt, *J* = 14.1, 7.5 Hz, 1H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.36 (t, *J* = 7.0 Hz, 3H), 1.25 (s, 9H), 0.94 (t, *J* = 7.4 Hz, 3H).

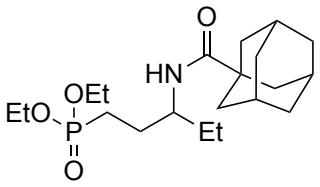
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 61.6 (d, *J* = 6.6 Hz), 50.6 (d, *J* = 16.7 Hz), 38.8, 27.9, 27.7, 27.5 (d, *J* = 4.6 Hz), 22.2 (d, *J* = 141.9 Hz), 16.5 (d, *J* = 6.0 Hz), 16.4 (d, *J* = 6.0 Hz), 10.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4.

FT-IR (film) 3325, 2966, 1642, 1538, 1238, 1032, 960, 798 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{31}NO_4P$: 308.1985, found: 308.1987.

$[\alpha]^{24}_D$ = –11 (*c* 1.0, $CHCl_3$); 90% ee from (*S*,*S*)-**N1***.



Diethyl (3-(adamantane-1-carboxamido)pentyl)phosphonate (Figure 2, entry 15). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and (3r,5r,7r)-adamantane-1-carboxamide (89.7 mg, 0.50 mmol) at –20 °C. The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S,S*)-**N1***: 145 mg, 75% yield, 91% ee; (*R,R*)-**N1***: 149 mg, 77% yield, 89% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (35% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.4 min (major), 3.6 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.50 (d, *J* = 9.0 Hz, 1H), 4.17 – 4.07 (m, 4H), 3.96 – 3.90 (m, 1H), 2.09 (s, 4H), 1.90 – 1.83 (m, 7H), 1.81 – 1.71 (m, 7H), 1.70 – 1.54 (m, 2H), 1.43 (dt, *J* = 14.1, 7.6 Hz, 1H), 1.363 (t, *J* = 7.0 Hz, 3H), 1.357 (t, *J* = 7.0 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H).

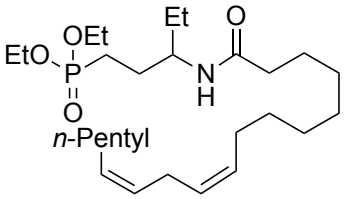
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 61.6 (d, *J* = 6.6 Hz), 50.3 (d, *J* = 17.4 Hz), 40.8, 39.4, 36.5, 28.2, 27.6 (d, *J* = 4.5 Hz), 22.3 (d, *J* = 141.9 Hz), 16.5 (d, *J* = 6.0 Hz), 16.4 (d, *J* = 6.0 Hz), 10.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4.

FT-IR (film) 3436, 3326, 2904, 1633, 1531, 1449, 1272, 1238, 1031, 964, 795 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{20}H_{37}NO_4P$: 386.2455, found: 386.2450.

$[\alpha]^{24}_D$ = +5.7 (*c* 1.0, $CHCl_3$); 91% ee from (*S,S*)-**N1***.



Diethyl (3-((9Z,12Z)-octadeca-9,12-dienamido)pentyl)phosphonate (Figure 2, entry 16). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and (9Z,12Z)-octadeca-9,12-dienamide (140 mg, 0.50 mmol) at –20 °C. The product was purified by flash column chromatography (EtOAc →10% MeOH/EtOAc). Pale yellow oil.

(*S,S*)-**N1***: 172 mg, 71% yield, 90% ee; (*R,R*)-**N1***: 180 mg, 74% yield, 89% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.3 min (major), 5.2 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (d, *J* = 9.1 Hz, 1H), 5.37 – 5.20 (m, 4H), 4.10 – 3.92 (m, 4H), 3.86 – 3.77 (m, 1H), 2.70 (t, *J* = 6.6 Hz, 2H), 2.14 – 2.07 (m, 2H), 1.98 (q, *J* = 6.8 Hz, 4H), 1.83 – 1.16 (m, 28H), 0.86 – 0.80 (m, 6H).

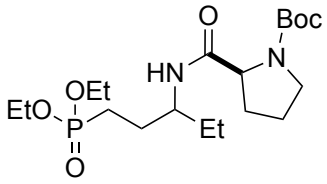
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 130.2, 130.1, 128.0, 127.9, 61.7 (d, *J* = 6.6 Hz), 61.6 (d, *J* = 6.6 Hz), 50.7 (d, *J* = 16.3 Hz), 37.0, 31.5, 29.6, 29.4, 29.33, 29.30, 29.2, 28.0, 27.4 (d, *J* = 4.5 Hz), 27.2, 25.9, 25.6, 22.6, 22.2 (d, *J* = 141.9 Hz), 16.5 (d, *J* = 5.3 Hz), 14.1, 10.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5.

FT-IR (film) 3286, 2930, 1714, 1643, 1538, 1454, 1234, 1030, 968, 754 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{27}H_{53}NO_4P$: 486.3707, found: 486.3719.

$[\alpha]^{24}_D$ = +14 (*c* 0.50, $CHCl_3$); 90% ee from (*S,S*)-**N1***.



***tert*-Butyl (2*S*)-2-((1-(diethoxyphosphoryl)pentan-3-yl)carbamoyl)pyrrolidine-1-carboxylate (Figure 2, entry 17).** The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and *tert*-butyl (*S*)-2-carbamoylpyrrolidine-1-carboxylate (107 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Pale yellow oil.

(*S,S*)-**N1***: 151 mg, 72% yield, 8:92 dr; (*R,R*)-**N1***: 106 mg, 51% yield, 93:7 dr.

The dr was determined via SFC on a CHIRALPAK ID-3 column (25% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 6.2 min (minor), 10.5 min (major).

Product obtained with (*S,S*)-**N1***:

^{1}H NMR (400 MHz, CD_3OD) δ 4.20 – 4.04 (m, 5H), 3.79 – 3.71 (m, 1H), 3.55 – 3.47 (m, 1H), 3.44 – 3.38 (m, 1H), 2.32 – 2.13 (m, 1H), 2.11 – 1.51 (m, 10H), 1.44 (s, 9H), 1.31 (t, *J* = 7.1 Hz, 6H), 0.91 (t, *J* = 6.1 Hz, 3H).

^{13}C NMR (101 MHz, CD_3OD) δ 174.4, 154.7, 79.8 (d, *J* = 56.8 Hz), 61.8 (d, *J* = 6.6 Hz), 60.4 (d, *J* = 10.7 Hz), 51.3 (d, *J* = 18.0 Hz), 46.7 (d, *J* = 26.2 Hz), 31.7, 30.3, 27.4, 27.0, 23.6 (d, *J* = 108.8 Hz), 21.9 (d, *J* = 141.6 Hz), 21.2 (d, *J* = 141.6 Hz), 15.4 (d, *J* = 6.1 Hz), 9.6 (d, *J* = 7.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4, 31.8.

FT-IR (film) 3472, 3298, 2970, 1677, 1548, 1396, 1240, 1170, 1030, 961, 775, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{19}H_{38}N_2O_6P$: 421.2462, found: 421.2465.

$[\alpha]^{24}_D$ = –56 (*c* 1.0, $CHCl_3$).

Product obtained with (*R,R*)-**N1***:

^{1}H NMR (400 MHz, CD_3OD) δ 4.22 – 4.01 (m, 5H), 3.79 – 3.71 (p, *J* = 4.7 Hz, 1H), 3.57 – 3.47 (m, 1H), 3.46 – 3.35 (m, 1H), 2.31 – 2.14 (m, 1H), 1.97 – 1.39 (m, 19H), 1.31 (td, *J* = 7.1, 1.4 Hz, 6H), 0.91 (t, *J* = 7.3 Hz, 3H).

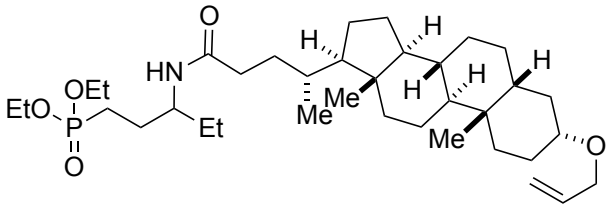
^{13}C NMR (101 MHz, CD_3OD) δ 174.4, 154.7, 79.8 (d, *J* = 56.6 Hz), 61.8 (d, *J* = 6.6 Hz), 60.4 (d, *J* = 10.6 Hz), 51.3 (d, *J* = 18.1 Hz), 46.7 (d, *J* = 26.4 Hz), 31.7, 30.3, 27.4, 27.0, 23.6 (d, *J* = 108.7 Hz), 21.9 (d, *J* = 141.6 Hz), 21.2 (d, *J* = 141.6 Hz), 15.4 (d, *J* = 6.1 Hz), 9.6 (d, *J* = 7.4 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3, 31.7.

FT-IR (film) 3410, 3287, 3062, 2954, 1651, 1538, 1455, 1361, 1242, 1024, 970, 847, 791, 740 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{19}H_{38}N_2O_6P$: 421.2462, found: 421.2466.

$[\alpha]^{24}_D$ = –29 (*c* 1.0, $CHCl_3$).



Diethyl (3-((*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-(allyloxy)-10,13-dimethyl hexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanamido)pentyl)phosphonate (Figure 2, entry 18). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and (*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-(allyloxy)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanamide (208 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Viscous oil.

(*S*,*S*)-**N1***: 227 mg, 73% yield, 95:5 dr; (*R*,*R*)-**N1***: 243 mg, 78% yield, 7:93 dr.

The dr was determined via SFC on a CHIRALPAK IG-3 column (30% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 7.3 min (major), 8.0 min (minor).

Product obtained with (*S*,*S*)-**N1***:

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.98 (ddt, *J* = 16.1, 10.7, 5.6 Hz, 1H), 5.59 (d, *J* = 9.1 Hz, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 4.19 – 4.09 (m, 4H), 4.07 (d, *J* = 5.6 Hz, 2H), 3.96 – 3.89 (m, 1H), 3.40 – 3.32 (m, 1H), 2.32 – 2.27 (m, 1H), 2.17 – 2.07 (m, 1H), 1.99 (d, *J* = 12.3 Hz, 1H), 1.96 – 1.76 (m, 9H), 1.72 – 1.57 (m, 4H), 1.51 – 1.22 (m, 19H), 1.19 – 1.05 (m, 5H), 1.03 – 0.90 (m, 9H), 0.68 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 135.6, 116.4, 78.6, 68.9, 61.7 (d, *J* = 6.5 Hz), 61.6 (d, *J* = 6.5 Hz), 56.5, 56.0, 50.7 (d, *J* = 16.5 Hz), 42.7, 42.1, 40.3, 40.2, 35.8, 35.5, 35.4, 34.9, 33.8, 33.2, 32.0, 28.3, 28.0, 27.4 (d, *J* = 4.4 Hz), 27.3, 27.2, 26.4, 24.2, 23.4, 22.2 (d, *J* = 141.9 Hz), 20.8, 18.4, 16.5 (d, *J* = 6.0 Hz), 12.0, 10.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5.

FT-IR (film) 3410, 3289, 2931, 1644, 1538, 1446, 1382, 1240, 1029, 966, 848, 754 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{36}H_{65}NO_5P$: 622.4595, found: 622.4591.

$[\alpha]^{24}_D$ = +28 (*c* 0.60, $CHCl_3$).

Product obtained with (*R*,*R*)-**N1***:

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.40 (d, *J* = 9.2 Hz, 1H), 5.20 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.08 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.11 – 3.91 (m, 6H), 3.85 – 3.76 (m, 1H), 3.27 – 3.20 (m, 1H), 2.21 – 2.14 (m, 1H), 2.05 – 1.96 (m, 1H), 1.90 – 1.84 (m, 1H), 1.83 – 1.64 (m, 9H), 1.61 – 1.41 (m, 4H), 1.41 – 1.11 (m, 19H), 1.08 – 0.92 (m, 5H), 0.89-0.82 (m, 9H), 0.56 (s, 3H).

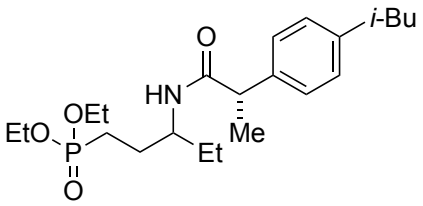
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 135.6, 116.4, 78.6, 69.0, 61.6 (d, *J* = 5.4 Hz), 56.5, 56.0, 50.7 (d, *J* = 16.6 Hz), 42.7, 42.1, 40.3, 40.2, 35.8, 35.5, 35.4, 34.9, 33.8, 33.2, 32.0, 28.3, 28.0, 27.4 (d, *J* = 4.4 Hz), 27.3, 27.2, 26.4, 24.2, 23.4, 22.3 (d, *J* = 141.9 Hz), 20.8, 18.4, 16.5 (d, *J* = 6.0 Hz), 12.1, 10.3.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.4.

FT-IR (film) 3434, 3286, 2932, 1644, 1538, 1446, 1378, 1239, 1031, 963, 753 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{36}H_{65}NO_5P$: 622.4595, found: 622.4590.

$[\alpha]^{24}_D$ = +17 (*c* 1.0, $CHCl_3$).



Diethyl (3-((*S*)-2-(4-isobutylphenyl)propanamido)pentyl)phosphonate (Figure 2, entry 19). The title compound was synthesized according to **GP-10** from diethyl (3-bromopentyl)phosphonate (172 mg, 0.60 mmol) and (*S*)-2-(4-isobutylphenyl)propanamide (103 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (EtOAc →10% MeOH/EtOAc). Pale yellow oil.

(*S,S*)-**N1***: 198 mg, 96% yield, 93:7 dr; (*R,R*)-**N1***: 194 mg, 94% yield, 8:92 dr.

The dr was determined via SFC on a CHIRALPAK ID-3 column (25% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 4.2 min (major), 4.6 min (minor).

Product obtained with (*S,S*)-**N1***:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.44 (d, *J* = 9.0 Hz, 1H), 4.11 – 3.96 (m, 4H), 3.89 – 3.84 (m, 1H), 3.58 (q, *J* = 7.1 Hz, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 1.91 – 1.85 (m, 1H), 1.83 – 1.72 (m, 1H), 1.68 – 1.45 (m, 7H), 1.40 – 1.28 (m, 7H), 0.93 (d, *J* = 6.6 Hz, 6H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 140.7, 138.8, 129.6, 127.2, 61.6 (d, *J* = 6.5 Hz), 61.5 (d, *J* = 6.5 Hz), 50.9 (d, *J* = 17.2 Hz), 46.8, 45.0, 30.2, 27.8, 27.5 (d, *J* = 4.5 Hz), 22.3 (d, *J* = 3.6 Hz), 22.2 (d, *J* = 141.9 Hz), 18.3, 16.4 (d, *J* = 6.0 Hz), 9.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.3.

FT-IR (film) 3410, 3280, 2963, 1651, 1538, 1236, 1030, 967, 848, 792 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{22}H_{39}NO_4P$: 412.2611, found: 412.2615.

$[\alpha]^{24}_D$ = +11 (*c* 1.0, $CHCl_3$).

Product obtained with (*R,R*)-**N1***:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.37 (d, *J* = 9.1 Hz, 1H), 4.13 – 4.06 (m, 4H), 3.89 – 3.82 (m, 1H), 3.58 (q, *J* = 7.1 Hz, 1H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.94 – 1.82 (m, 1H), 1.83 – 1.69 (m, 3H), 1.63 – 1.52 (m, 4H), 1.52 – 1.43 (m, 1H), 1.39 – 1.22 (m, 7H), 0.95 – 0.91 (m, 6H), 0.73 (t, *J* = 7.4 Hz, 3H).

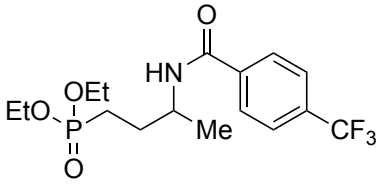
^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 140.6, 138.7, 129.6, 127.2, 61.5 (d, *J* = 6.6 Hz), 50.8 (d, *J* = 17.2 Hz), 46.9, 45.0, 30.2, 27.8, 27.4 (d, *J* = 4.5 Hz), 22.4, 21.9 (d, *J* = 141.6 Hz), 18.5, 16.4 (dd, *J* = 6.0, 2.0 Hz), 10.2.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.2.

FT-IR (film) 3410, 3287, 2954, 1652, 1539, 1361, 1242, 1024, 970, 846, 791 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{22}H_{39}NO_4P$: 412.2611, found: 412.2614.

$[\alpha]^{24}_D$ = +17 (*c* 1.0, $CHCl_3$).



Diethyl (3-(4-(trifluoromethyl)benzamido)butyl)phosphonate (Figure 3, entry 20). The title compound was synthesized according to **GP-10** from diethyl (3-bromobutyl)phosphonate (164 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S*,*S*)-**N1***: 185 mg, 97% yield, 92% ee; (*R*,*R*)-**N1***: 179 mg, 94% yield, 92% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 1.6 min (major), 2.1 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 1H), 4.23 – 4.16 (m, 1H), 4.07 – 3.97 (m, 2H), 3.97 – 3.88 (m, 2H), 1.91 – 1.64 (m, 4H), 1.29 – 1.13 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 137.9, 132.9 (q, *J* = 32.6 Hz), 127.7, 125.4 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 61.8 (d, *J* = 6.6 Hz), 46.1 (d, *J* = 13.6 Hz), 28.7 (d, *J* = 4.5 Hz), 21.9 (d, *J* = 141.6 Hz), 20.4, 16.4 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 6.1 Hz).

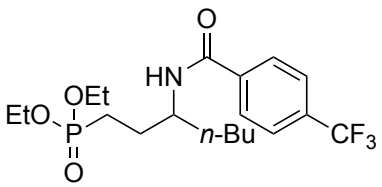
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3444, 3304, 2986, 1646, 1551, 1322, 1243, 960, 860, 681 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{24}F_3NO_4P$: 382.1390, found: 382.1387.

$[\alpha]^{24}_D$ = +0.5 (*c* 1.0, $CHCl_3$); 92% ee from (*S*,*S*)-**N1***.



Diethyl (3-(4-(trifluoromethyl)benzamido)heptyl)phosphonate (Figure 3, entry 21). The title compound was synthesized according to **GP-10** from diethyl (3-bromoheptyl)phosphonate (189 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg,

0.50 mmol). The product was purified by flash column chromatography (66% EtOAc/hexane→EtOAc→3% MeOH/EtOAc). Colorless oil.

(*S,S*)-**N1***: 166 mg, 78% yield, 91% ee; (*R,R*)-**N1***: 158 mg, 74% yield, 91% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10.0% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.8 min (minor), 5.4 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 1H), 4.18 – 4.08 (m, 1H), 4.08 – 3.96 (m, 2H), 3.96 – 3.87 (m, 2H), 1.97 – 1.65 (m, 4H), 1.59 – 1.45 (m, 2H), 1.34 – 1.21 (m, 7H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.89 – 0.77 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 137.9, 133.0 (q, *J* = 32.6 Hz), 127.6, 125.4 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.4 Hz), 61.8 (d, *J* = 6.6 Hz), 50.0 (d, *J* = 12.9 Hz), 34.4, 28.2, 27.2 (d, *J* = 4.5 Hz), 22.6, 21.8 (d, *J* = 141.5 Hz), 16.4 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 6.1 Hz), 14.0.

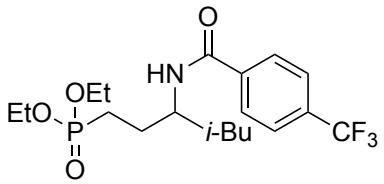
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3443, 3302, 3067, 2932, 1646, 1551, 1323, 1240, 968, 860, 826, 686 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{19}H_{30}F_3NO_4P$: 424.1859, found: 424.1857.

$[\alpha]^{24}_D$ = –0.7 (*c* 1.0, $CHCl_3$); 91% ee from (*S,S*)-**N1***.



Diethyl (5-methyl-3-(4-(trifluoromethyl)benzamido)hexyl)phosphonate (Figure 3, entry 22). The title compound was synthesized according to **GP-10** from diethyl (3-bromo-5-methylhexyl)phosphonate (189 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (66% EtOAc/hexane→EtOAc→3% MeOH/EtOAc). Colorless oil.

(*S,S*)-**N1***: 142 mg, 67% yield, 84% ee; (*R,R*)-**N1***: 135 mg, 64% yield, 84% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.2 min (major), 4.5 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 1H), 4.31 – 4.22 (m, 1H), 4.09 – 3.97 (m, 2H), 3.97 – 3.88 (m, 2H), 1.97 – 1.67 (m, 4H), 1.67 – 1.54 (m, 1H), 1.51 – 1.44 (m, 1H), 1.36 – 1.23 (m, 4H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.88 – 0.87 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 137.8, 133.1 (q, *J* = 32.6 Hz), 127.6, 125.5 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 61.82 (d, *J* = 6.6 Hz), 61.80 (d, *J* = 6.6 Hz), 48.0 (d, *J* = 12.5 Hz), 44.0, 27.9 (d, *J* = 4.5 Hz), 24.0 (d, *J* = 217.4 Hz), 22.4, 21.0, 16.4 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 6.0 Hz).

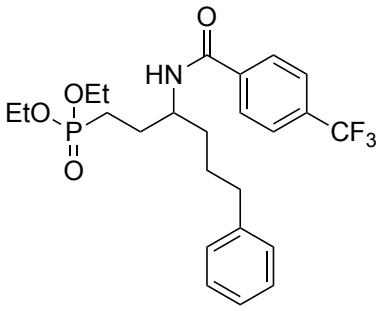
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3442, 3280, 2958, 1643, 1554, 1327, 1231, 1170, 1129, 1066, 968, 862 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{19}H_{30}F_3NO_4P$: 424.1859, found: 424.1859.

$[\alpha]^{24}_D$ = +0.2 (*c* 1.0, $CHCl_3$); 84% ee from (*R,R*)-**N1***.



Diethyl (6-phenyl-3-(4-(trifluoromethyl)benzamido)hexyl)phosphonate (Figure 3, entry 23). The title compound was synthesized according to **GP-10** from diethyl (3-bromo-6-phenylhexyl)phosphonate (226 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (25% acetone/hexane →33% acetone/hexane). Colorless oil.

(*S,S*)-**N1***: 171 mg, 70% yield, 91% ee; (*R,R*)-**N1***: 178 mg, 73% yield, 91% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 8.2 min (major), 11.3 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.24 – 7.14 (m, 4H), 4.32 – 4.22 (m, 1H), 4.15 – 4.04 (m, 2H), 4.04 – 3.95 (m, 2H), 2.74 – 2.60 (m, 2H), 2.07 – 1.59 (m, 8H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 142.0, 137.8, 133.0 (q, *J* = 32.6 Hz), 128.42, 128.37, 127.7, 125.9, 125.5 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 61.8 (d, *J* = 6.6 Hz), 49.8 (d, *J* = 12.6 Hz), 35.6, 34.2, 27.9, 27.2 (d, *J* = 4.5 Hz), 21.7 (d, *J* = 141.5 Hz), 16.4 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 6.0 Hz).

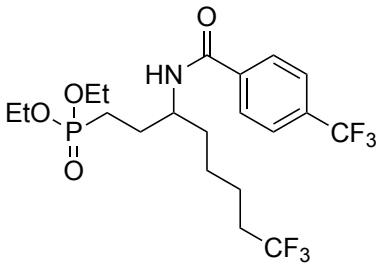
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3436, 3288, 2931, 1646, 1550, 1454, 1324, 1240, 1123, 1019, 967, 858, 751, 683 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{24}H_{32}F_3NO_4P$: 486.2016, found: 486.2020.

$[\alpha]^{24}_D$ = –1.8 (*c* 1.0, $CHCl_3$); 91% ee from (*S,S*)-**N1***.



Diethyl (8,8,8-trifluoro-3-(4-(trifluoromethyl)benzamido)octyl)phosphonate (Figure 3, entry 24). The title compound was synthesized according to **GP-10** from diethyl (3-bromo-

8,8,8-trifluorooctyl)phosphonate (230 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane→33% acetone/hexane). Colorless oil.

(*S,S*)-**N1***: 178 mg, 72% yield, 91% ee; (*R,R*)-**N1***: 169 mg, 69% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.1 min (major), 3.4 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 1H), 4.21 – 4.12 (m, 1H), 4.11 – 3.97 (m, 2H), 3.96 – 3.87 (m, 2H), 2.09 – 1.67 (m, 6H), 1.63 – 1.46 (m, 4H), 1.44 – 1.34 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 137.6, 133.1 (q, *J* = 32.6 Hz), 127.7, 127.1 (q, *J* = 276.4 Hz), 125.5 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 61.9 (d, *J* = 6.7 Hz), 49.7 (d, *J* = 11.3 Hz), 34.4, 33.6 (q, *J* = 28.4 Hz), 27.0 (d, *J* = 4.5 Hz), 25.3, 21.8 (d, *J* = 2.9 Hz), 21.7 (d, *J* = 141.6 Hz), 16.4 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 6.0 Hz).

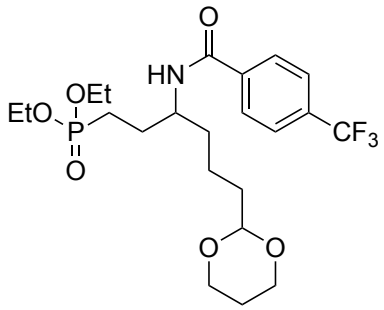
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0, –66.4.

FT-IR (film) 3443, 3279, 2944, 1644, 1556, 1392, 1327, 1253, 1164, 1028, 860, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{20}H_{29}F_6NO_4P$: 492.1733, found: 492.1731.

$[\alpha]^{24}_D$ = –1.8 (*c* 1.0, $CHCl_3$); 91% ee from (*S,S*)-**N1***.



Diethyl (6-(1,3-dioxan-2-yl)-3-(4-(trifluoromethyl)benzamido)hexyl)phosphonate (Figure 3, entry 25). The title compound was synthesized according to **GP-10** from diethyl (3-bromo-6-(1,3-dioxan-2-yl)hexyl)phosphonate (232 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S,S*)-**N1***: 175 mg, 71% yield, 91% ee; (*R,R*)-**N1***: 179 mg, 72% yield, 91% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 7.8 min (major), 11.2 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 1H), 4.34 (t, *J* = 4.8 Hz, 1H), 4.18 – 4.08 (m, 1H), 4.07 – 3.97 (m, 4H), 3.96 – 3.88 (m, 2H), 3.70 – 3.63 (m, 2H), 2.06 – 1.66 (m, 6H), 1.62 – 1.49 (m, 4H), 1.45 – 1.37 (m, 2H), 1.28 – 1.23 (m, 4H), 1.16 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 137.8, 133.0 (q, *J* = 32.6 Hz), 127.6, 125.5 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 102.0, 66.9, 61.9 (d, *J* = 6.6 Hz), 61.8 (d, *J* = 6.6 Hz), 50.1 (d, *J* = 12.7 Hz), 34.9, 34.4, 27.1 (d, *J* = 4.5 Hz), 25.8, 21.7 (d, *J* = 141.6 Hz), 20.5, 16.4 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 6.0 Hz).

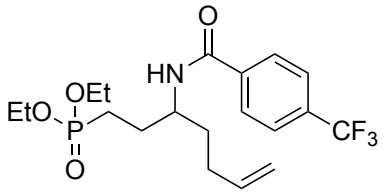
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3466, 3298, 2916, 1646, 1551, 857, 680 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{22}H_{34}F_3NO_6P$: 496.2070, found: 496.2065.

$[\alpha]^{24}_D$ = +2.4 (*c* 1.0, $CHCl_3$); 91% ee from (*S*,*S*)-**N1***.



Diethyl (3-(4-(trifluoromethyl)benzamido)hept-6-en-1-yl)phosphonate (Figure 3, entry 26). The title compound was synthesized according to **GP-10** from diethyl (3-bromohept-6-en-1-yl)phosphonate (230 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (EtOAc). Colorless oil.

(*S*,*S*)-**N1***: 169 mg, 80% yield, 91% ee; (*R*,*R*)-**N1***: 175 mg, 83% yield, 91% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 5.1 min (major), 7.9 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.9 Hz, 1H), 5.84 (ddt, *J* = 16.8, 10.2, 6.6 Hz, 1H), 5.10 – 4.96 (m, 2H), 4.31 – 4.21 (m, 1H), 4.19 – 4.05 (m, 2H), 4.05 – 3.95 (m, 2H), 2.16 (q, *J* = 7.6 Hz, 2H), 2.08 – 1.65 (m, 7H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 137.7, 133.0 (q, *J* = 32.6 Hz), 127.6, 125.5 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 115.3, 61.9 (d, *J* = 6.6 Hz), 49.6 (d, *J* = 12.5 Hz), 33.8, 30.3, 27.1 (d, *J* = 4.5 Hz), 21.7 (d, *J* = 141.6 Hz), 16.4 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 6.1 Hz).

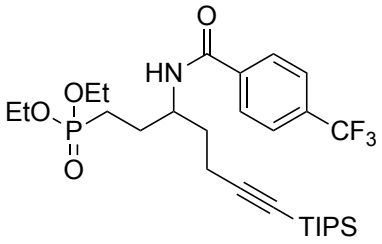
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3290, 2930, 1645, 1549, 1454, 1325, 1219, 1132, 1065, 1019, 960, 861, 680 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{19}H_{28}F_3NO_4P$: 422.1703, found: 422.1707.

$[\alpha]^{24}_D$ = –1.6 (*c* 1.0, $CHCl_3$); 91% ee from (*S*,*S*)-**N1***.



Diethyl (3-(4-(trifluoromethyl)benzamido)-7-(triisopropylsilyl)hept-6-yn-1-yl)phosphonate (Figure 3, entry 27). The title compound was synthesized according to **GP-10** from diethyl (3-bromo-7-(triisopropylsilyl)hept-6-yn-1-yl)phosphonate (281 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). Colorless oil.

(*S*,*S*)-**N1***: 189 mg, 66% yield, 88% ee; (*R*,*R*)-**N1***: 174 mg, 60% yield, 88% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 3.8 min (major), 4.5 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 1H), 4.26 – 4.18 (m, 1H), 4.10 – 3.97 (m, 2H), 3.97 – 3.86 (m, 2H), 1.97 – 1.66 (m, 7H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.03 – 0.86 (m, 22H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 137.7, 133.1 (q, *J* = 32.7 Hz), 127.7, 125.5 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 107.8, 81.0, 61.9 (d, *J* = 4.8 Hz), 49.8 (d, *J* = 12.1 Hz), 33.9, 26.8 (d, *J* = 4.5 Hz), 21.8 (d, *J* = 141.6 Hz), 18.6, 17.0, 16.4 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 6.1 Hz), 11.2.

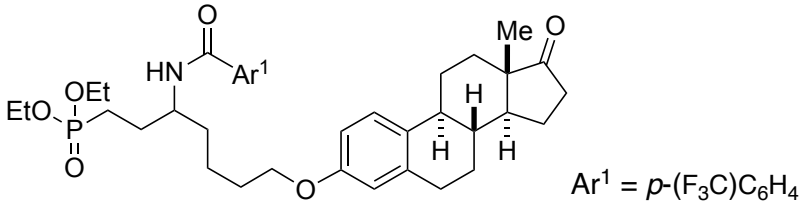
^{31}P NMR (162 MHz, $CDCl_3$) δ 32.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3288, 2941, 2172, 1652, 1549, 1462, 1324, 1238, 1126, 1022, 964, 858, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{28}H_{46}F_3NO_4PSi$: 576.2880, found: 576.2876.

$[\alpha]^{24}_D$ = +1.1 (*c* 1.0, $CHCl_3$); 88% ee from (*S*,*S*)-**N1***.



Diethyl (7-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)-3-(4-(trifluoromethyl)benzamido)heptyl)phosphonate (Figure 3, entry 28). The title compound was synthesized according to **GP-10** from diethyl (3-bromo-7-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)heptyl)phosphonate (350 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane→33% acetone/hexane). White solid.

(*S*,*S*)-**N1***: 221 mg, 64% yield, 96:4 dr; (*R*,*R*)-**N1***: 233 mg, 68% yield, 4:96 dr.

The dr was determined via SFC on a CHIRALPAK AD-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 9.6 min (major), 11.7 min (minor).

Product obtained with (*S,S*)-**N1***:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 9.8 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 1H), 6.59 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.52 (d, *J* = 2.6 Hz, 1H), 4.22 – 4.12 (m, 1H), 4.09 – 3.96 (m, 2H), 3.96 – 3.88 (m, 2H), 3.84 (td, *J* = 6.2, 2.8 Hz, 2H), 2.81 – 2.77 (m, 2H), 2.42 (dd, *J* = 18.7, 8.5 Hz, 1H), 2.35 – 2.26 (m, 1H), 2.18 – 2.12 (m, 1H), 2.11 – 1.67 (m, 11H), 1.65 – 1.30 (m, 9H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 157.0, 137.78, 137.77, 137.7, 133.0 (q, *J* = 32.6 Hz), 132.0, 127.7, 126.3, 125.4 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 114.5, 112.1, 67.5, 61.9 (d, *J* = 6.7 Hz), 61.8 (d, *J* = 6.7 Hz), 50.4, 49.9 (d, *J* = 12.8 Hz), 48.0, 44.0, 38.4, 35.9, 34.4, 31.6, 29.6, 29.1, 27.2 (d, *J* = 4.4 Hz), 26.5, 25.9, 22.7, 21.8 (d, *J* = 141.6 Hz), 21.6, 16.4 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 6.0 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3284, 2931, 1736, 1653, 1543, 1500, 1327, 1236, 1164, 1128, 1066, 966, 755, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{37}H_{50}F_3NO_6P$: 692.3322, found: 692.3340.

$[\alpha]^{24}_D$ = +68 (*c* 1.0, $CHCl_3$).

m.p.: 115-117 °C.

Product obtained with (*R,R*)-**N1***:

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.68 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.61 (d, *J* = 2.6 Hz, 1H), 4.30 – 4.20 (m, 1H), 4.18 – 4.05 (m, 2H), 4.04 – 3.96 (m, 2H), 3.93 (t, *J* = 6.3 Hz, 2H), 2.95 – 2.80 (m, 2H), 2.50 (dd, *J* = 18.7, 8.5 Hz, 1H), 2.44 – 2.32 (m, 1H), 2.27 – 2.21 (m, 1H), 2.20 – 1.75 (m, 11H), 1.74 – 1.39 (m, 9H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 157.0, 137.78, 137.77, 137.7, 133.0 (q, *J* = 32.6 Hz), 132.0, 127.7, 126.3, 125.4 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 114.5, 112.1, 67.5, 61.9 (d, *J* = 6.7 Hz), 50.4, 49.9 (d, *J* = 13.0 Hz), 48.0, 44.0, 38.4, 35.9, 34.4, 31.6, 29.6, 29.1, 27.2 (d, *J* = 4.4 Hz), 26.5, 25.9, 22.7, 21.8 (d, *J* = 141.5 Hz), 21.6, 16.4 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 6.0 Hz), 13.9.

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.7.

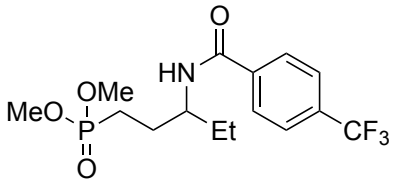
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3289, 2932, 1731, 1644, 1538, 1504, 1327, 1240, 1130, 1032, 969, 858, 753 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{37}H_{50}F_3NO_6P$: 692.3322, found: 692.3300.

$[\alpha]^{24}_D$ = +62 (*c* 1.0, $CHCl_3$).

m.p.: 72-75 °C.



Dimethyl (3-(4-(trifluoromethyl)benzamido)pentyl)phosphonate (Figure 3, entry 29). The title compound was synthesized according to **GP-10** from dimethyl (3-bromopentyl)phosphonate (156 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (EtOAc→10% MeOH/EtOAc). Colorless oil.

(*S,S*)-**N1***: 171 mg, 93% yield, 90% ee; (*R,R*)-**N1***: 162 mg, 88% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 2.2 min (major), 2.6 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 1H), 4.20 – 4.07 (m, 1H), 3.74 (d, *J* = 10.8 Hz, 3H), 3.65 (d, *J* = 10.8 Hz, 3H), 2.02 – 1.75 (m, 4H), 1.68 – 1.58 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 137.8, 133.0 (q, *J* = 32.6 Hz), 127.6, 125.5 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 52.5 (d, *J* = 6.8 Hz), 51.5 (d, *J* = 13.7 Hz), 27.6, 26.7 (d, *J* = 4.5 Hz), 20.9 (d, *J* = 141.6 Hz), 10.4.

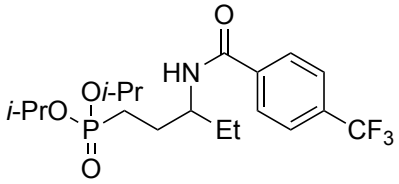
^{31}P NMR (162 MHz, $CDCl_3$) δ 35.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3312, 2964, 1645, 1550, 1311, 1240, 1019, 840, 680 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{15}H_{22}F_3NO_4P$: 368.1233, found: 368.1234.

$[\alpha]^{24}_D$ = +2.9 (*c* 0.70, $CHCl_3$); 90% ee from (*S,S*)-**N1***.



Diisopropyl (3-(4-(trifluoromethyl)benzamido)pentyl)phosphonate (Figure 3, entry 30). The title compound was synthesized according to **GP-10** from diisopropyl (3-bromopentyl)phosphonate (189 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (66% EtOAc/hexane→ EtOAc). Colorless oil.

(*S,S*)-**N1***: 206 mg, 97% yield, 88% ee; (*R,R*)-**N1***: 202 mg, 95% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.4 min (major), 4.0 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 1H), 4.68 (ddt, *J* = 12.4, 7.9, 6.2 Hz, 1H), 4.56 (ddt, *J* = 12.4, 7.9, 6.2 Hz, 1H), 4.21 – 4.09 (m,

1H), 2.03 – 1.93 (m, 1H), 1.92 – 1.69 (m, 3H), 1.65 (p, *J* = 7.4 Hz, 2H), 1.33 (d, *J* = 6.2 Hz, 3H), 1.32 (d, *J* = 6.2 Hz, 3H), 1.26 (d, *J* = 6.2 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 138.0, 132.9 (q, *J* = 32.6 Hz), 127.7, 125.4 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.4 Hz), 70.4 (d, *J* = 6.8 Hz), 70.3 (d, *J* = 6.8 Hz), 51.4 (d, *J* = 12.3 Hz), 27.5, 26.6 (d, *J* = 4.6 Hz), 24.1 (d, *J* = 4.3 Hz), 24.0 (d, *J* = 4.3 Hz), 23.9 (d, *J* = 3.8 Hz), 23.0 (d, *J* = 142.8 Hz), 10.4.

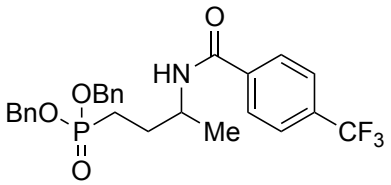
^{31}P NMR (162 MHz, $CDCl_3$) δ 30.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3436, 3285, 2978, 1651, 1556, 1324, 1234, 1110, 1016, 889, 860, 770, 683 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{19}H_{30}F_3NO_4P$: 424.1859, found: 424.1858.

$[\alpha]^{24}_D$ = –3.4 (*c* 1.0, $CHCl_3$); 88% ee from (*S*,*S*)-**N1***.



Dibenzyl (3-(4-(trifluoromethyl)benzamido)butyl)phosphonate (Figure 3, entry 31). The title compound was synthesized according to **GP-10** from dibenzyl (3-bromobutyl)phosphonate (238 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (25% acetone/hexane →33% acetone/hexane). Colorless oil.

(*S*,*S*)-**N1***: 201 mg, 81% yield, 89% ee; (*R*,*R*)-**N1***: 185 mg, 74% yield, 89% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (25% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 3.4 min (major), 4.4 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.24 (m, 10H), 7.21 (d, *J* = 8.2 Hz, 1H), 5.13 – 4.80 (m, 4H), 4.28 – 4.15 (m, 1H), 1.99 – 1.73 (m, 4H), 1.24 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 137.8, 136.1 (d, *J* = 5.7 Hz), 136.0 (d, *J* = 5.7 Hz), 133.0 (q, *J* = 32.6 Hz), 128.7 (d, *J* = 5.3 Hz), 128.6 (d, *J* = 5.5 Hz), 127.9 (d, *J* = 15.5 Hz), 127.7, 125.4 (q, *J* = 3.7 Hz), 123.8 (d, *J* = 272.5 Hz), 67.5 (d, *J* = 5.9 Hz), 67.4 (d, *J* = 5.9 Hz), 46.1 (d, *J* = 14.0 Hz), 28.6 (d, *J* = 4.5 Hz), 22.4 (d, *J* = 141.0 Hz), 20.5.

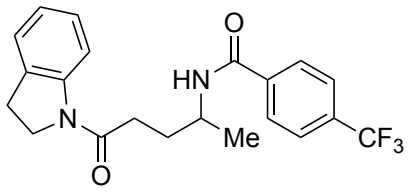
^{31}P NMR (162 MHz, $CDCl_3$) δ 33.9.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3288, 2969, 1645, 1547, 1456, 1328, 1244, 1170, 1128, 1067, 1017, 861, 734, 696 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{26}H_{28}F_3NO_4P$: 506.1703, found: 506.1700.

$[\alpha]^{24}_D$ = –14 (*c* 1.0, $CHCl_3$); 89% ee from (*S*,*S*)-**N1***.



***N*-(5-(Indolin-1-yl)-5-oxopentan-2-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 32).** The title compound was synthesized according to **GP-11** from 4-bromo-1-(indolin-1-yl)pentan-1-one (169 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N2***: 166 mg, 85% yield, 89% ee; (*R,R*)-**N2***: 163 mg, 84% yield, 88% ee.

The ee was determined via HPLC on a CHIRALPAK AD-H column (20% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 8.1 min (major), 15.7 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 6.9 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 4.29 – 4.21 (m, 1H), 4.11 – 4.05 (m, 2H), 3.29 – 3.08 (m, 2H), 2.75 – 2.56 (m, 2H), 2.32 – 2.25 (m, 1H), 2.04 – 1.99 (m, 1H), 1.40 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 165.5, 142.6, 137.6, 132.8 (q, *J* = 32.6 Hz), 131.2, 127.5, 127.4, 125.3 (q, *J* = 3.7 Hz), 124.7, 124.1, 123.7 (q, *J* = 272.5 Hz), 116.9, 48.0, 47.3, 33.0, 29.7, 27.9, 21.4.

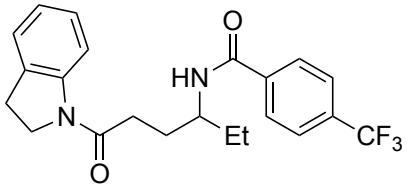
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3298, 2970, 1636, 1542, 1483, 1411, 1327, 1162, 1119, 1067, 1017, 855, 756, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{21}H_{22}F_3N_2O_2$: 391.1628, found: 391.1627.

$[\alpha]^{24}_D$ = +49 (*c* 1.0, $CHCl_3$); 89% ee from (*S,S*)-**N2***.

m.p.: 153 °C.



***N*-(6-(Indolin-1-yl)-6-oxohexan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 33).** The title compound was synthesized according to **GP-11** from 4-bromo-1-(indolin-1-yl)hexan-1-one (178 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N2***: 159 mg, 79% yield, 93% ee; (*R,R*)-**N2***: 165 mg, 82% yield, 92% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 5.3 min (major), 6.5 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.05 (t, *J* = 7.0 Hz, 2H), 4.18 – 4.12 (m, 1H), 4.11 – 4.01 (m, 2H), 3.26 – 3.06 (m, 2H), 2.74 – 2.53 (m, 2H), 2.32 – 2.21 (m, 1H), 2.04 (ddt, *J* = 14.6, 7.3, 3.6 Hz, 1H), 1.75 (p, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 165.8, 142.6, 137.5, 132.8 (q, *J* = 32.6 Hz), 131.1, 127.4, 127.3, 125.3 (q, *J* = 3.8 Hz), 124.6, 124.0, 123.7 (q, *J* = 272.5 Hz), 116.9, 52.5, 48.0, 32.9, 28.6, 27.9, 27.4, 10.3.

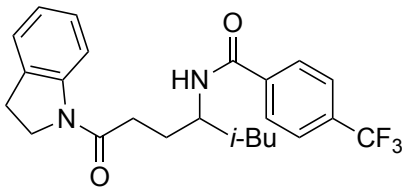
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3292, 2966, 1639, 1542, 1483, 1410, 1327, 1125, 1067, 850, 754, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{22}H_{24}F_3N_2O_2$: 405.1784, found: 405.1784.

$[\alpha]^{24}_D$ = –64 (*c* 1.0, $CHCl_3$); 93% ee from (*R,R*)-**N2***.

m.p.: 146 °C.



***N*-(1-(Indolin-1-yl)-6-methyl-1-oxoheptan-4-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 34).** The title compound was synthesized according to **GP-11** from 4-bromo-1-(indolin-1-yl)-6-methylheptan-1-one (195 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N2***: 125 mg, 58% yield, 93% ee; (*R,R*)-**N2***: 131 mg, 61% yield, 94% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (25% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 3.6 min (major), 4.6 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.21 – 7.11 (m, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 1H), 4.39 – 4.30 (m, 1H), 4.12 – 3.99 (m, 2H), 3.22 – 3.04 (m, 2H), 2.69 – 2.55 (m, 2H), 2.28 – 2.17 (m, 1H), 2.07 – 2.01 (m, 1H), 1.80 – 1.72 (m, 1H), 1.67 – 1.62 (m, 1H), 1.52 – 1.46 (m, 1H), 1.03 (dd, *J* = 11.0, 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 165.6, 142.6, 137.4, 132.8 (q, *J* = 32.6 Hz), 131.1, 127.4, 127.2, 125.3 (q, *J* = 3.7 Hz), 124.6, 123.9, 123.7 (q, *J* = 272.6 Hz), 116.9, 49.1, 48.0, 45.3, 32.7, 28.8, 27.8, 25.1, 22.8, 22.7.

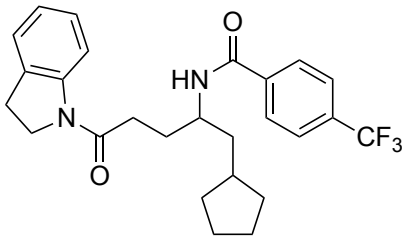
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3305, 2958, 1639, 1544, 1483, 1411, 1327, 1170, 1128, 1067, 1018, 860, 755, 669 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{24}H_{28}F_3N_2O_2$: 433.2097, found: 433.2092.

$[\alpha]^{24}_D$ = +44 (*c* 1.3, $CHCl_3$); 93% ee from (*S,S*)-**N2***.

m.p.: 92 °C.



***N*-(1-Cyclopentyl-5-(indolin-1-yl)-5-oxopentan-2-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 35).** The title compound was synthesized according to **GP-11** from 4-bromo-5-cyclopentyl-1-(indolin-1-yl)pentan-1-one (210 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N2***: 151 mg, 66% yield, 94% ee; (*R,R*)-**N2***: 139 mg, 60% yield, 93% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (25% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 6.9 min (major), 11.7 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.20 – 7.10 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 4.31 – 4.25 (m, 1H), 4.11 – 3.98 (m, 2H), 3.22 – 3.04 (m, 2H), 2.68 – 2.56 (m, 2H), 2.30 – 2.18 (m, 1H), 2.12 – 2.02 (m, 1H), 1.97 – 1.91 (m, 2H), 1.88 – 1.82 (m, 1H), 1.80 – 1.75 (m, 1H), 1.72 – 1.64 (m, 3H), 1.63 – 1.51 (m, 2H), 1.29 – 1.15 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 165.6, 142.6, 137.5, 132.8 (q, *J* = 32.5 Hz), 131.1, 127.4, 127.3, 125.3 (q, *J* = 3.8 Hz), 124.6, 124.0, 123.7 (q, *J* = 272.5 Hz), 116.9, 50.5, 48.0, 42.3, 37.1, 33.2, 32.8, 28.6, 27.9, 25.2, 25.1.

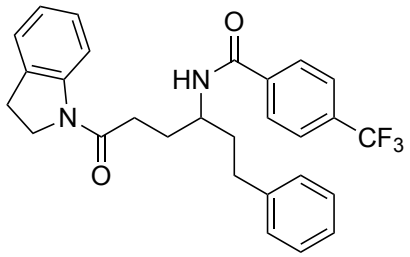
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3315, 2950, 1639, 1543, 1482, 1410, 1327, 1170, 1127, 1066, 1017, 860, 754, 670 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{26}H_{30}F_3N_2O_2$: 459.2254, found: 459.2253.

$[\alpha]^{24}_D$ = +52 (*c* 1.0, $CHCl_3$); 94% ee from (*S,S*)-**N2***.

m.p.: 146 °C.



***N*-(6-(Indolin-1-yl)-6-oxo-1-phenylhexan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 36).** The title compound was synthesized according to **GP-11** from 4-bromo-1-(indolin-1-yl)-6-phenylhexan-1-one (223 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N2***: 161 mg, 65% yield, 95% ee; (*R,R*)-**N2***: 168 mg, 68% yield, 94% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (25% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 8.3 min (major), 9.4 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.1 Hz, 2H), 7.27 (d, *J* = 7.0 Hz, 2H), 7.25 – 7.13 (m, 3H), 7.08 – 7.00 (m, 2H), 4.36 – 4.27 (m, 1H), 4.05 (dp, *J* = 9.9, 3.2 Hz, 2H), 3.24 – 3.06 (m, 2H), 2.81 (p, *J* = 7.5 Hz, 2H), 2.72 – 2.54 (m, 2H), 2.39 – 2.28 (m, 1H), 2.14 – 1.98 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 165.7, 142.6, 141.7, 137.3, 132.8 (q, *J* = 34.9 Hz), 131.1, 128.5, 128.4, 127.4, 127.3, 126.0, 125.3 (q, *J* = 3.8 Hz), 124.6, 124.0, 123.7 (q, *J* = 262.7 Hz), 116.9, 50.9, 48.0, 37.4, 32.8, 32.3, 28.1, 27.9.

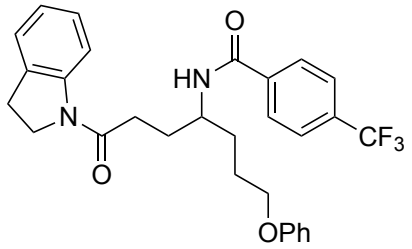
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3304, 2916, 1634, 1538, 1484, 1417, 1328, 1162, 1120, 1066, 858, 750 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{28}H_{28}F_3N_2O_2$: 481.2097, found: 481.2090.

$[\alpha]^{24}_D$ = +38 (*c* 1.0, $CHCl_3$); 95% ee from (*S,S*)-**N2***.

m.p.: 170 °C.



***N*-(1-(Indolin-1-yl)-1-oxo-7-phenoxyheptan-4-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 37).** The title compound was synthesized according to **GP-11** from 4-bromo-1-(indolin-1-yl)-7-phenoxyheptan-1-one (241 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N2***: 167 mg, 65% yield, 94% ee; (*R,R*)-**N2***: 173 mg, 67% yield, 94% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (25% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 8.7 min (major), 10.9 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.22 – 7.15 (m, 2H), 7.10 – 7.00 (m, 3H), 6.92 (td, *J* = 7.4, 0.9 Hz, 1H), 6.88 – 6.79 (m, 3H), 4.22 – 4.12 (m, 1H), 3.98 – 3.89 (m, 4H), 3.09 – 2.93 (m, 2H), 2.63 – 2.40 (m, 2H), 2.24 – 2.13 (m, 1H), 1.98 – 1.90 (m, 1H), 1.89 – 1.70 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 165.9, 158.9, 142.6, 137.3, 132.9 (q, *J* = 32.5 Hz), 131.1, 129.5, 127.4, 127.3, 125.3 (q, *J* = 3.7 Hz), 124.6, 124.1, 123.7 (q, *J* = 272.6 Hz), 120.7, 116.9, 114.5, 67.4, 50.7, 48.0, 32.8, 32.4, 28.1, 27.9, 25.8.

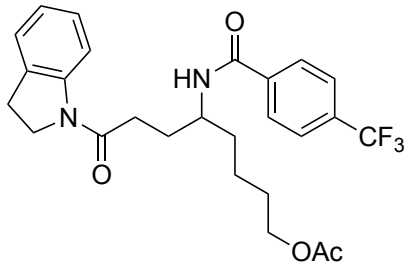
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3292, 2942, 1644, 1599, 1540, 1483, 1412, 1328, 1245, 1124, 1066, 754, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{29}H_{30}F_3N_2O_3$: 511.2203, found: 511.2201.

$[\alpha]^{24}_D$ = +37 (*c* 1.3, $CHCl_3$); 94% ee from (*S*,*S*)-**N2***.

m.p.: 155 °C.



8-(Indolin-1-yl)-8-oxo-5-(4-(trifluoromethyl)benzamido)octyl acetate (Figure 3, entry 38). The title compound was synthesized according to **GP-11** from 5-bromo-8-(indolin-1-yl)-8-oxooctyl acetate (229 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane→33% acetone/hexane). White solid.

(*S*,*S*)-**N2***: 175 mg, 71% yield, 95% ee; (*R*,*R*)-**N2***: 179 mg, 73% yield, 95% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (30% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N2***: 3.0 min (major), 3.8 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.10 – 7.01 (m, 2H), 6.97 (d, *J* = 8.3 Hz, 1H), 6.92 (td, *J* = 7.4, 0.9 Hz, 1H), 4.12 – 4.05 (m, 1H), 4.01 – 3.96 (m, 2H), 3.95 – 3.89 (m, 2H), 3.10 – 2.94 (m, 2H), 2.61 – 2.38 (m, 2H), 2.21 – 2.07 (m, 1H), 1.95 (s, 4H), 1.64 – 1.55 (m, 4H), 1.44 – 1.36 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 171.2, 165.7, 142.6, 137.3, 132.9 (q, *J* = 32.5 Hz), 131.1, 127.4, 127.3, 125.3 (q, *J* = 3.8 Hz), 124.6, 124.1, 123.7 (q, *J* = 272.6 Hz), 116.9, 64.2, 51.0, 48.0, 35.4, 32.8, 28.6, 27.93, 27.86, 22.4, 21.0.

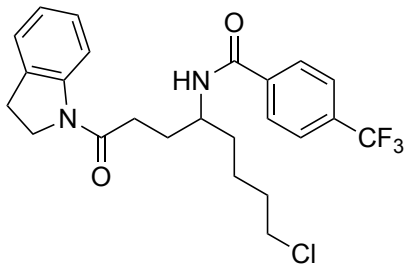
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3308, 2943, 2860, 1732, 1651, 1538, 1484, 1416, 1329, 1248, 1168, 1122, 1068, 856, 759, 684 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{26}H_{30}F_3N_2O_4$: 491.2152, found: 491.2160.

$[\alpha]^{24}_D$ = +49 (*c* 1.0, $CHCl_3$); 95% ee from (*S*,*S*)-**N2***.

m.p.: 116 °C.



***N*-(8-Chloro-1-(indolin-1-yl)-1-oxooctan-4-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 39).** The title compound was synthesized according to **GP-11** from 4-bromo-8-chloro-1-(indolin-1-yl)octan-1-one (215 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N2***: 159 mg, 68% yield, 92% ee; (*R,R*)-**N2***: 168 mg, 72% yield, 92% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (25% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 5.7 min (major), 7.1 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.11 – 7.01 (m, 3H), 6.93 (td, *J* = 7.5, 0.9 Hz, 1H), 4.13 – 4.04 (m, 1H), 3.97 – 3.87 (m, 2H), 3.52 – 3.43 (m, 2H), 3.11 – 2.94 (m, 2H), 2.62 – 2.40 (m, 2H), 2.20 – 2.10 (m, 1H), 1.95 – 1.89 (m, 1H), 1.80 – 1.72 (m, 2H), 1.66 – 1.56 (m, 2H), 1.56 – 1.43 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 165.8, 142.6, 137.3, 132.9 (q, *J* = 32.6 Hz), 131.1, 127.5, 127.3, 125.3 (q, *J* = 3.8 Hz), 124.7, 124.1, 123.7 (q, *J* = 272.6 Hz), 116.9, 50.9, 48.0, 44.9, 34.9, 32.8, 32.3, 27.9, 27.7, 23.1.

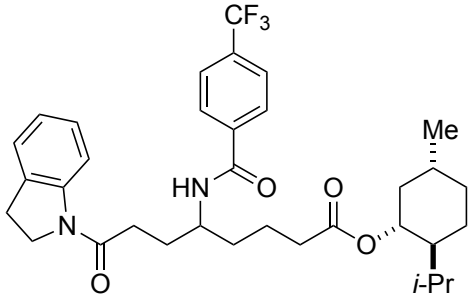
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3422, 3274, 2922, 1646, 1541, 1482, 1458, 1412, 1329, 1123, 1066, 844, 757, 681 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{24}H_{27}ClF_3N_2O_2$: 467.1708, found: 467.1710.

$[\alpha]^{24}_D$ = +52 (*c* 1.0, $CHCl_3$); 92% ee from (*S,S*)-**N2***.

m.p.: 165 °C.



(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 8-(indolin-1-yl)-8-oxo-5-(4-(trifluoromethyl)benzamido)octanoate (Figure 3, entry 40). The title compound was synthesized according to **GP-11** from (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 5-bromo-8-(indolin-1-yl)-8-oxooctanoate (296 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg,

0.50 mmol). The product was purified by flash column chromatography (33% EtOAc/hexane→ 50% EtOAc /hexane). White solid.

(*S,S*)-**N2***: 175 mg, 58% yield, 95:5 dr; (*R,R*)-**N2***: 197 mg, 66% yield, 6:94 dr.

The dr was determined via SFC on a CHIRALPAK AD-3 column (30% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 2.9 min (major), 6.3 min (minor).

Product obtained with (*S,S*)-**N2*:**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.11 – 7.01 (m, 3H), 6.92 (td, *J* = 7.4, 0.9 Hz, 1H), 4.60 (td, *J* = 10.9, 4.4 Hz, 1H), 4.15 – 4.02 (m, 1H), 3.92 (t, *J* = 8.5 Hz, 2H), 3.11 – 2.92 (m, 2H), 2.61 – 2.40 (m, 2H), 2.28 (t, *J* = 6.9 Hz, 2H), 2.21 – 2.07 (m, 1H), 1.95 – 1.87 (m, 2H), 1.79 – 1.70 (m, 1H), 1.70 – 1.56 (m, 6H), 1.45 – 1.37 (m, 1H), 1.31 – 1.24 (m, 1H), 1.04 – 0.86 (m, 2H), 0.81 (dd, *J* = 13.3, 6.8 Hz, 7H), 0.66 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 171.8, 165.8, 142.6, 137.4, 132.8 (q, *J* = 32.6 Hz), 131.1, 127.43, 127.36, 125.3 (q, *J* = 3.8 Hz), 124.6, 124.0, 123.7 (q, *J* = 272.4 Hz), 116.9, 74.1, 50.8, 48.0, 47.0, 41.0, 35.0, 34.26, 34.25, 32.8, 31.4, 27.92, 27.87, 26.3, 23.4, 22.0, 21.3, 20.7, 16.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3314, 2955, 1726, 1644, 1540, 1483, 1412, 1327, 1170, 1130, 1067, 1017, 859, 755, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{34}H_{44}F_3N_2O_4$: 601.3248, found: 601.3250.

$[\alpha]^{24}_D$ = +3.7 (*c* 1.0, $CHCl_3$).

m.p.: 147-148 °C.

Product obtained with (*R,R*)-**N2*:**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.10 – 7.03 (m, 3H), 6.92 (td, *J* = 7.4, 0.8 Hz, 1H), 4.60 (td, *J* = 10.9, 4.4 Hz, 1H), 4.15 – 4.02 (m, 1H), 3.92 (t, *J* = 8.5 Hz, 2H), 3.12 – 2.91 (m, 2H), 2.63 – 2.39 (m, 2H), 2.27 (t, *J* = 6.5 Hz, 2H), 2.21 – 2.07 (m, 1H), 1.97 – 1.84 (m, 2H), 1.81 – 1.73 (m, 1H), 1.70 – 1.56 (m, 6H), 1.43 – 1.36 (m, 1H), 1.31 – 1.24 (m, 1H), 1.04 – 0.85 (m, 2H), 0.81 (dd, *J* = 6.8, 2.8 Hz, 7H), 0.68 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 171.8, 165.7, 142.6, 137.4, 132.8 (q, *J* = 32.6 Hz), 131.1, 127.43, 127.36, 125.3 (q, *J* = 3.7 Hz), 124.6, 124.0, 123.7 (q, *J* = 272.6 Hz), 116.7, 74.2, 50.8, 48.0, 47.0, 41.0, 35.0, 34.3, 34.2, 32.8, 31.4, 27.93, 27.87, 26.3, 23.4, 22.0, 21.4, 20.8, 16.4.

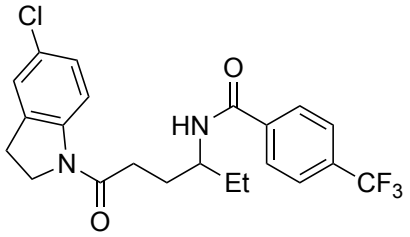
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3312, 2955, 1727, 1652, 1538, 1483, 1412, 1327, 1171, 1130, 1067, 1017, 860, 755, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{34}H_{44}F_3N_2O_4$: 601.3248, found: 601.3245.

$[\alpha]^{24}_D$ = –64 (*c* 1.0, $CHCl_3$).

m.p.: 103-104 °C.



***N*-(6-(5-Chloroindolin-1-yl)-6-oxohexan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 41).** The title compound was synthesized according to **GP-11** from 4-bromo-1-(5-chloroindolin-1-yl)hexan-1-one (198 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N2***: 165 mg, 75% yield, 92% ee; (*R,R*)-**N2***: 174 mg, 79% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 8.1 min (major), 10.2 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.17 – 7.08 (m, 2H), 6.85 (d, *J* = 8.3 Hz, 1H), 4.20 – 4.13 (m, 1H), 4.12 – 4.02 (m, 2H), 3.25 – 3.05 (m, 2H), 2.72 – 2.53 (m, 2H), 2.28 – 2.17 (m, 1H), 2.05 (ddt, *J* = 14.8, 7.5, 3.9 Hz, 1H), 1.82 – 1.67 (m, 2H), 1.05 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 165.7, 141.3, 137.4, 133.02, 132.97 (q, *J* = 32.6 Hz), 128.9, 127.4, 127.3, 125.3 (q, *J* = 3.8 Hz), 125.0 (q, *J* = 278.3 Hz), 124.8, 117.6, 52.3, 48.2, 32.8, 28.6, 27.8, 27.7, 10.3.

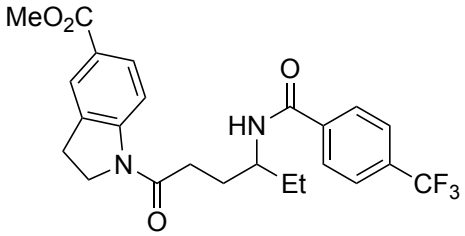
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3302, 2932, 1636, 1535, 1471, 1402, 1328, 1161, 1119, 1067, 852, 682 cm^{-1}.

HRMS (LC-MS) *m/z* $(M+H)^+$ calcd for $C_{22}H_{23}ClF_3N_2O_2$: 439.1395, found: 439.1399.

$[\alpha]^{24}_D$ = +54 (*c* 0.60, $CHCl_3$); 92% ee from (*S,S*)-**N2***.

m.p.: 190-191°C.



Methyl 1-(4-(4-(trifluoromethyl)benzamido)hexanoyl)indoline-5-carboxylate (Figure 3, entry 42). The title compound was synthesized according to **GP-11** from methyl 1-(4-bromohexanoyl)indoline-5-carboxylate (221 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N2***: 160 mg, 69% yield, 88% ee; (*R,R*)-**N2***: 166 mg, 72% yield, 88% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 8.8 min (major), 11.7 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.82 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 6.76 (d, *J* = 8.5 Hz, 1H), 4.23 – 4.04 (m, 3H), 3.95 (s, 3H), 3.26 – 3.10 (m, 2H), 2.71 – 2.58 (m, 2H), 2.27 – 2.19 (m, 1H), 2.11 – 2.04 (m, 1H), 1.80 – 1.68 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 166.7, 165.7, 146.5, 137.3, 133.0 (q, *J* = 32.8 Hz), 131.3, 130.0, 127.2, 126.0, 125.6, 125.3 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 272.6 Hz), 116.1, 52.3, 52.0, 48.5, 33.0, 28.7, 27.9, 27.4, 10.3.

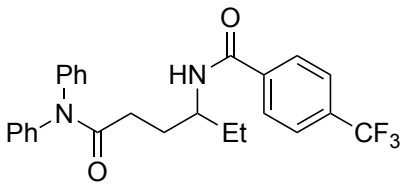
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3309, 2958, 1714, 1652, 1538, 1487, 1445, 1402, 1327, 1275, 1164, 1126, 1067, 858, 770 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{24}H_{26}F_3N_2O_4$: 463.1839, found: 463.1838.

$[\alpha]^{24}_D$ = +66 (*c* 1.0, $CHCl_3$); 88% ee from (*S,S*)-**N2***.

m.p.: 178 °C.



***N*-(6-(Diphenylamino)-6-oxohexan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 43).** The title compound was synthesized according to **GP-11** from 4-bromo-*N,N*-diphenylhexanamide (208 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (33% EtOAc/hexane). White solid.

(*S,S*)-**N2***: 143 mg, 63% yield, 91% ee; (*R,R*)-**N2***: 139 mg, 61% yield, 91% ee.

The ee was determined via SFC on a CHIRALPAK IC-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 3.2 min (minor), 4.0 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.06 (m, 10H), 6.99 (d, *J* = 8.2 Hz, 1H), 4.08 – 4.01 (m, 1H), 2.53 – 2.36 (m, 2H), 2.16 – 2.05 (m, 1H), 1.97 – 1.91 (m, 1H), 1.68 (p, *J* = 7.3 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 165.6, 142.4, 137.8, 132.9 (q, *J* = 32.5 Hz), 130.0, 128.9, 128.6, 128.2, 127.6, 126.5, 125.5 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.4 Hz), 52.2, 32.4, 28.5, 28.0, 10.1.

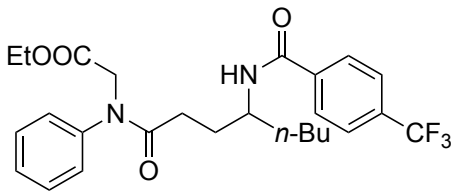
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3236, 2933, 1652, 1540, 1493, 1326, 1124, 1066, 849, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{26}H_{26}F_3N_2O_2$: 455.1941, found: 455.1935.

$[\alpha]^{24}_D$ = –52 (*c* 0.60, $CHCl_3$); 91% ee from (*S,S*)-**N2***.

m.p.: 110 °C.



Ethyl *N*-phenyl-*N*-(4-(4-(trifluoromethyl)benzamido)octanoyl)glycinate (Figure 3, entry 44). The title compound was synthesized according to **GP-11** from ethyl *N*-(4-bromooctanoyl)-*N*-phenylglycinate (231 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N2***: 122 mg, 49% yield, 91% ee; (*R,R*)-**N2***: 126 mg, 51% yield, 91% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 4.1 min (major), 6.5 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.40 (dq, *J* = 14.5, 7.1 Hz, 3H), 7.34 – 7.28 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 4.38 – 4.26 (m, 2H), 4.21 – 4.11 (m, 2H), 4.07 – 3.96 (m, 1H), 2.42 – 2.22 (m, 2H), 2.02 – 1.89 (m, 2H), 1.69 – 1.54 (m, 2H), 1.41 – 1.31 (m, 4H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 168.9, 165.5, 142.4, 138.1, 132.8 (q, *J* = 32.6 Hz), 129.9, 128.6, 128.0, 127.5, 125.4 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.5 Hz), 61.3, 51.4, 50.7, 35.1, 31.0, 28.3, 28.0, 22.6, 14.1, 14.0.

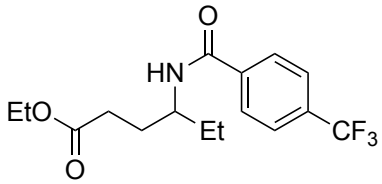
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3312, 2931, 1748, 1652, 1597, 1539, 1496, 1392, 1327, 1200, 1129, 1067, 1018, 861, 760, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{26}H_{32}F_3N_2O_4$: 493.2309, found: 493.2312.

$[\alpha]^{24}_D$ = –44 (*c* 0.50, $CHCl_3$); 91% ee from (*S,S*)-**N2***.

m.p.: 30 °C.



Ethyl 4-(4-(trifluoromethyl)benzamido)hexanoate (Figure 3, entry 45). The title compound was synthesized according to **GP-12** from ethyl 4-bromohexanoate (134 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% EtOAc/hexane). White solid.

(*S,S*)-**N2***: 130 mg, 78% yield, 87% ee; (*R,R*)-**N2***: 124 mg, 74% yield, 87% ee.

The ee was determined via HPLC on a CHIRALPAK AD-H column (10% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**L2**: 7.6 min (major), 13.1 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 6.42 (d, *J* = 8.4 Hz, 1H), 4.19 – 4.04 (m, 3H), 2.60 – 2.40 (m, 2H), 2.08 – 1.86 (m, 2H), 1.78 – 1.61 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 165.8, 137.9, 133.1 (q, *J* = 32.7 Hz), 127.4, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 60.7, 51.6, 31.1, 28.8, 28.2, 14.1, 10.3.

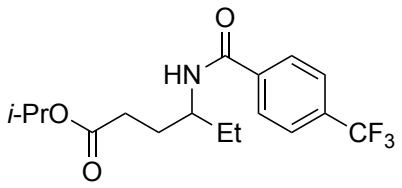
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3290, 2965, 1731, 1644, 1548, 1449, 1327, 1166, 1128, 1109, 1068, 1017, 859, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{21}F_3NO_3$: 332.1468, found: 332.1471.

$[\alpha]^{24}_D$ = –0.8 (*c* 1.0, $CHCl_3$); 87% ee from (*S*,*S*)-**N2***.

m.p.: 93 °C.



Isopropyl 4-(4-(trifluoromethyl)benzamido)hexanoate (Figure 3, entry 46). The title compound was synthesized according to **GP-12** from isopropyl 4-bromohexanoate (142 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% EtOAc/hexane). White solid.

(*S*,*S*)-**N2***: 153 mg, 89% yield, 87% ee; (*R*,*R*)-**N2***: 160 mg, 93% yield, 87% ee.

The ee was determined via HPLC on a CHIRALPAK AD-H column (10% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**N2***: 6.4 min (major), 9.4 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 6.52 (d, *J* = 8.5 Hz, 1H), 4.99 (hept, *J* = 6.3 Hz, 1H), 4.12 (dtt, *J* = 10.0, 6.9, 3.6 Hz, 1H), 2.55 – 2.38 (m, 2H), 2.04 – 1.87 (m, 2H), 1.77 – 1.60 (m, 2H), 1.26 (d, *J* = 6.2 Hz, 3H), 1.16 (d, *J* = 6.3 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 165.8, 137.9, 133.1 (q, *J* = 32.7 Hz), 127.4, 125.5 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 68.1, 51.6, 31.4, 28.7, 28.2, 21.8, 21.7, 10.3.

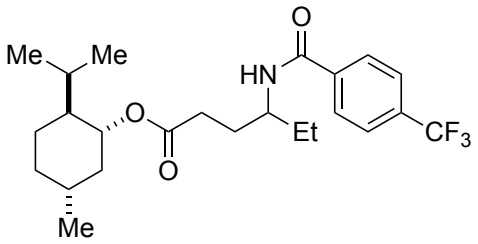
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3299, 2972, 1728, 1644, 1548, 1454, 1375, 1328, 1171, 1131, 1068, 1018, 858, 770, 688 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{23}F_3NO_3$: 346.1625, found: 346.1621.

$[\alpha]^{24}_D$ = –3.0 (*c* 1.0, $CHCl_3$); 87% ee from (*S*,*S*)-**N2***.

m.p.: 94 °C.



(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-(4-(trifluoromethyl)benzamido)hexanoate (Figure 3, entry 47). The title compound was synthesized according to **GP-12** from (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 4-bromohexanoate (199 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (10% EtOAc/hexane). White solid.

(*S*,*S*)-**N2***: 172 mg, 78% yield, 95:5 dr; (*R*,*R*)-**N2***: 184 mg, 83% yield, 8:92 dr.

The dr was determined via HPLC on a CHIRALPAK AD-H column (10% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S*,*S*)-**N2***: 5.0 min (major), 7.8 min (minor).

Product obtained with (*S*,*S*)-**N2***:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 6.50 (d, *J* = 8.6 Hz, 1H), 4.69 (td, *J* = 10.9, 4.3 Hz, 1H), 4.19 – 4.08 (m, 1H), 2.56 (dt, *J* = 17.1, 6.7 Hz, 1H), 2.46 – 2.40 (m, 1H), 2.04 – 1.91 (m, 2H), 1.87 (pd, *J* = 7.0, 2.7 Hz, 1H), 1.78 – 1.61 (m, 5H), 1.46 – 1.30 (m, 2H), 1.09 (td, *J* = 12.5, 2.6 Hz, 1H), 1.03 (t, *J* = 7.4 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.91 – 0.83 (m, 2H), 0.80 (dd, *J* = 6.7, 2.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 165.6, 137.7, 133.1 (q, *J* = 32.7 Hz), 127.4, 125.5 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 74.7, 51.8, 46.9, 40.8, 34.1, 31.4, 31.3, 28.5, 28.3, 26.3, 23.4, 21.8, 20.7, 16.3, 10.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3334, 2959, 1728, 1641, 1538, 1456, 1328, 1170, 1131, 1068, 1018, 858, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{24}H_{35}F_3NO_3$: 442.2564, found: 442.2564.

$[\alpha]^{24}_D$ = –51 (*c* 1.0, $CHCl_3$).

m.p.: 132-133 °C.

Product obtained with (*R*,*R*)-**N2***:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 1H), 4.69 (td, *J* = 10.9, 4.4 Hz, 1H), 4.16 – 4.08 (m, 1H), 2.54 (dt, *J* = 16.9, 7.0 Hz, 1H), 2.44 (dt, *J* = 17.0, 6.9 Hz, 1H), 2.03 – 1.97 (m, 2H), 1.94 – 1.86 (m, 1H), 1.83 – 1.61 (m, 6H), 1.56 – 1.48 (m, 1H), 1.43 – 1.33 (m, 1H), 1.13 – 0.84 (m, 11H), 0.62 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 165.8, 137.9, 133.1 (q, *J* = 32.7 Hz), 127.4, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 74.7, 51.7, 46.9, 40.9, 34.2, 31.36, 31.35, 28.6, 28.1, 26.2, 23.4, 22.0, 20.6, 16.1, 10.2.

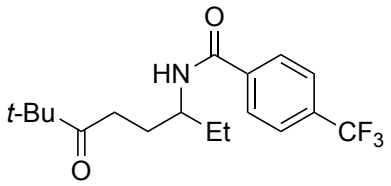
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3313, 2958, 1731, 1644, 1538, 1454, 1328, 1174, 1131, 1068, 1018, 860, 765, 681 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{24}H_{35}F_3NO_3$: 442.2564, found: 442.2559.

$[\alpha]^{24}_D$ = –39 (*c* 1.0, $CHCl_3$).

m.p.: 103-104 °C.



***N*-(7,7-Dimethyl-6-oxooctan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 48).** The title compound was synthesized according to **GP-10** from 6-bromo-2,2-dimethyloctan-3-one (141 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (10% acetone/hexane). White solid.

(*S,S*)-**N1***: 143 mg, 83% yield, 92% ee; (*R,R*)-**N1***: 140 mg, 81% yield, 92% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 2.7 min (major), 3.8 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 1H), 4.09 – 4.02 (m, 1H), 2.79 (ddd, *J* = 18.5, 7.1, 5.6 Hz, 1H), 2.65 (ddd, *J* = 18.5, 7.4, 5.6 Hz, 1H), 2.00 – 1.83 (m, 2H), 1.74 – 1.61 (m, 2H), 1.14 (s, 9H), 1.02 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.4, 165.6, 137.8, 133.1 (q, *J* = 32.7 Hz), 127.3, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 52.1, 44.2, 33.8, 28.6, 27.3, 26.5, 10.2.

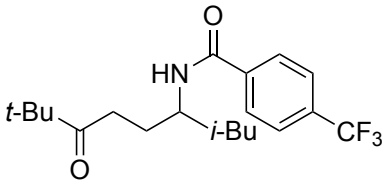
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3310, 2968, 1704, 1641, 1543, 1478, 1327, 1170, 1131, 1067, 1018, 859, 772, 681 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{18}H_{25}F_3NO_2$: 344.1832, found: 344.1840.

$[\alpha]^{24}_D$ = –6.9 (*c* 1.0, $CHCl_3$); 92% ee from (*S,S*)-**N1***.

m.p.: 57 °C.



4-(Trifluoromethyl)-*N*-(2,8,8-trimethyl-7-oxononan-4-yl)benzamide (Figure 3, entry 49). The title compound was synthesized according to **GP-10** from 6-bromo-2,2,8-trimethylnonan-3-one (158 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (10% acetone/hexane). White solid.

(*S,S*)-**N1***: 113 mg, 61% yield, 95% ee; (*R,R*)-**N1***: 117 mg, 63% yield, 94% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 2.4 min (major), 2.8 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 6.30 (d, *J* = 8.9 Hz, 1H), 4.28 – 4.20 (m, 1H), 2.77 (dt, *J* = 18.4, 6.5 Hz, 1H), 2.65 (dt, *J* = 18.4, 6.5 Hz, 1H), 1.89 (q, *J* = 6.8 Hz, 2H), 1.78 – 1.66 (m, 1H), 1.58 – 1.52 (m, 1H), 1.46 – 1.41 (m, 1H), 1.13 (s, 9H), 1.01 (dd, *J* = 9.7, 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.1, 165.5, 137.8, 133.1 (q, *J* = 32.7 Hz), 127.3, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 48.8, 45.5, 44.2, 33.6, 28.6, 26.5, 25.1, 22.9, 22.6.

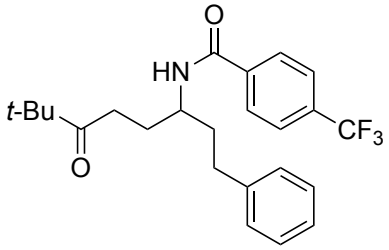
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3290, 2959, 1705, 1639, 1548, 1327, 1170, 1130, 1068, 1018, 862, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{20}H_{29}F_3NO_2$: 372.2145, found: 372.2150.

$[\alpha]^{24}_D$ = –1.0 (*c* 1.0, $CHCl_3$); 95% ee from (*S*,*S*)-**N1***.

m.p.: 64 °C.



***N*-(7,7-Dimethyl-6-oxo-1-phenyloctan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 50).** The title compound was synthesized according to **GP-10** from 6-bromo-2,2-dimethyl-8-phenyloctan-3-one (187 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (10% acetone/hexane). White solid.

(*S*,*S*)-**N1***: 128 mg, 61% yield, 94% ee; (*R*,*R*)-**N1***: 130 mg, 62% yield, 95% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 5.3 min (major), 8.9 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.21 (m, 3H), 6.47 (d, *J* = 8.6 Hz, 1H), 4.26 – 4.19 (m, 1H), 2.85 – 2.72 (m, 3H), 2.68 – 2.62 (m, 1H), 2.11 – 1.88 (m, 4H), 1.14 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.2, 165.6, 141.7, 137.6, 133.1 (q, *J* = 32.6 Hz), 128.5, 128.3, 127.3, 126.0, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 50.7, 44.2, 37.4, 33.7, 32.3, 27.9, 26.5.

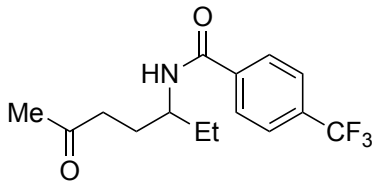
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3314, 2926, 1704, 1644, 1538, 1327, 1170, 1131, 1067, 1018, 861, 752, 681 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{24}H_{28}F_3NO_2$: 420.2145, found: 420.2145.

$[\alpha]^{24}_D$ = –13 (*c* 1.0, $CHCl_3$); 94% ee from (*S*,*S*)-**N1***.

m.p.: 117 °C.



***N*-(6-Oxoheptan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 51).** The title compound was synthesized according to **GP-10** from 6-bromo-2,2-dimethyl-8-phenyloctan-3-one (139 mg, 0.72 mmol) and 4-(trifluoromethyl)benzamide (107 mg, 0.60 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N1***: 134 mg, 74% yield, 91% ee; (*R,R*)-**N1***: 130 mg, 72% yield, 92% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 2.9 min (major), 3.2 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 6.48 (d, *J* = 8.3 Hz, 1H), 4.11 – 4.00 (m, 1H), 2.71 (dt, *J* = 18.4, 6.6 Hz, 1H), 2.60 (dt, *J* = 18.4, 6.6 Hz, 1H), 2.17 (s, 3H), 1.95 – 1.84 (m, 2H), 1.73 – 1.58 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 209.7, 165.9, 137.8 (q, *J* = 1.0 Hz), 133.1 (q, *J* = 32.7 Hz), 127.3, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 51.8, 40.6, 30.2, 28.4, 27.6, 10.3.

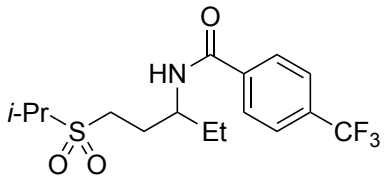
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3283, 1709, 1640, 1543, 1328, 1160, 1122, 859, 740 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{15}H_{19}F_3NO_2$: 302.1362, found: 302.1360.

$[\alpha]^{24}_D$ = –1.9 (*c* 1.0, $CHCl_3$); 91% ee from (*S,S*)-**N1***.

m.p.: 166 °C.



***N*-(1-(Isopropylsulfonyl)pentan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 52).** The title compound was synthesized according to **GP-13** from 3-bromo-1-(isopropylsulfonyl)pentane (193 mg, 0.75 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% EtOAc/hexane→ 25% EtOAc/hexane). White solid.

(*S,S*)-**N1***: 114 mg, 62% yield, 92% ee; (*R,R*)-**N1***: 112 mg, 61% yield, 92% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 4.3 min (major), 10.2 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 6.58 (d, *J* = 8.9 Hz, 1H), 4.15 – 4.05 (m, 1H), 3.14 – 2.97 (m, 2H), 2.97 – 2.86 (m, 1H), 2.19 – 2.10 (m, 1H), 2.04 – 1.94 (m, 1H), 1.71 – 1.50 (m, 2H), 1.28 (dd, *J* = 6.9, 4.8 Hz, 6H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 137.5, 133.3 (q, *J* = 32.7 Hz), 127.7, 125.6 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.6 Hz), 53.5, 50.5, 46.0, 28.2, 25.9, 15.4, 15.3, 10.4.

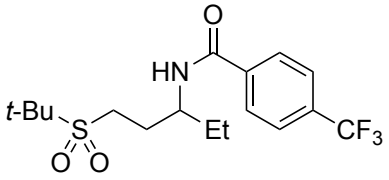
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3308, 2965, 1643, 1544, 1329, 1306, 1264, 1169, 1130, 1110, 1067, 855, 760, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{16}H_{23}F_3NO_3S$: 366.1345, found: 366.1343.

$[\alpha]^{24}_D$ = +2.5 (*c* 1.0, $CHCl_3$); 92% ee from (*S,S*)-**N1***.

m.p.: 143 °C.



***N*-(1-(*tert*-Butylsulfonyl)pentan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 53).** The title compound was synthesized according to **GP-13** from 3-bromo-1-(*tert*-butylsulfonyl)pentane (203 mg, 0.75 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% EtOAc/hexane). White solid.

(*S,S*)-**N1***: 119 mg, 73% yield, 96% ee; (*R,R*)-**N1***: 133 mg, 70% yield, 97% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 4.2 min (major), 7.5 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 6.68 (d, *J* = 9.0 Hz, 1H), 4.17 – 4.04 (m, 1H), 3.09 – 3.02 (m, 1H), 2.97 – 2.85 (m, 1H), 2.24 – 2.11 (m, 1H), 2.06 – 1.97 (m, 1H), 1.70 – 1.54 (m, 2H), 1.29 (s, 9H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 137.6, 133.2 (q, *J* = 32.7 Hz), 127.5, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 59.1, 50.7, 42.6, 28.4, 25.4, 23.4, 10.4.

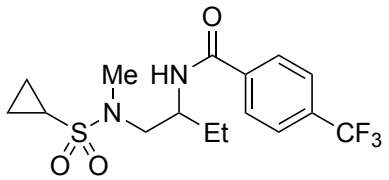
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3332, 2969, 1644, 1538, 1327, 1290, 1171, 1115, 1067, 1018, 860, 757, 660 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{25}F_3NO_3S$: 380.1502, found: 380.1506.

$[\alpha]^{24}_D$ = –2.9 (*c* 1.0, $CHCl_3$); 97% ee from (*R,R*)-**N1***.

m.p.: 87 °C.



***N*-(1-(*N*-Methylcyclopropanesulfonamido)butan-2-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 54).** The title compound was synthesized according to **GP-10** from *N*-(2-bromobutyl)-*N*-methylcyclopropanesulfonamide (162 mg, 0.60 mmol) and 4-

(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (20% acetone/hexane→33% acetone/hexane). White solid.

(*S,S*)-**N1***: 167 mg, 88% yield, 90% ee; (*R,R*)-**N1***: 172 mg, 91% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.6 min (major), 8.1 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.85 (m, 2H), 7.66 – 7.58 (m, 2H), 6.60 (d, *J* = 7.8 Hz, 1H), 4.23 – 4.11 (m, 1H), 3.46 (dd, *J* = 14.4, 9.7 Hz, 1H), 3.12 (dd, *J* = 14.4, 4.1 Hz, 1H), 2.91 (s, 3H), 2.24 (tt, *J* = 8.0, 4.9 Hz, 1H), 1.71 – 1.51 (m, 2H), 1.17 – 1.04 (m, 2H), 1.04 – 0.86 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 137.7, 133.1 (q, *J* = 32.6 Hz), 127.5, 125.6 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.6 Hz), 52.9, 49.2, 35.9, 27.4, 25.6, 10.1, 4.6, 4.5.

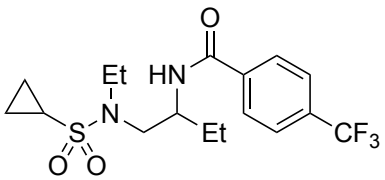
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3314, 2968, 1647, 1543, 1458, 1327, 1129, 1067, 890, 760, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* (M+H)$^+$ calcd for $C_{16}H_{22}F_3N_2O_3S$: 379.1298, found: 379.1330.

$[\alpha]^{24}_D$ = +13 (*c* 1.0, $CHCl_3$); 90% ee from (*S,S*)-**N1***.

m.p.: 154 °C.



***N*-(1-(*N*-Ethylcyclopropanesulfonamido)butan-2-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 55).** The title compound was synthesized according to **GP-10** from *N*-(2-bromobutyl)-*N*-ethylcyclopropanesulfonamide (171 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (20% acetone/hexane→40% acetone/hexane). White solid.

(*S,S*)-**N1***: 170 mg, 86% yield, 89% ee; (*R,R*)-**N1***: 176 mg, 89% yield, 89% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.6 min (major), 4.8 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.67 – 7.54 (m, 2H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.20 – 4.11 (m, 1H), 3.47 (dd, *J* = 14.9, 10.7 Hz, 1H), 3.37 – 3.25 (m, 2H), 3.18 (dd, *J* = 14.9, 4.2 Hz, 1H), 2.23 (tt, *J* = 8.0, 4.9 Hz, 1H), 1.69 – 1.49 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.15 – 1.08 (m, 2H), 0.99 – 0.88 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 137.7, 133.0 (q, *J* = 32.6 Hz), 127.6, 125.6 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.6 Hz), 49.6, 49.4, 43.0, 29.7, 25.8, 14.1, 10.0, 5.3, 5.2.

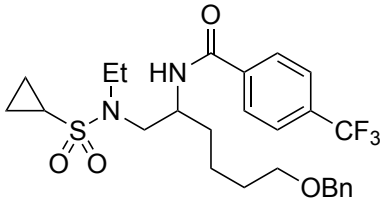
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3357, 2971, 1646, 1540, 1327, 1138, 1067, 1018, 860, 748, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* (M+H)$^+$ calcd for $C_{17}H_{24}F_3N_2O_3S$: 393.1454, found: 393.1454.

$[\alpha]^{24}_D$ = +18 (*c* 1.0, $CHCl_3$); 89% ee from (*S,S*)-**N1***.

m.p.: 130 °C.



***N*-(6-(Benzyloxy)-1-(*N*-ethylcyclopropanesulfonamido)hexan-2-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 56).** The title compound was synthesized according to **GP-10** from *N*-(6-(benzyloxy)-2-bromohexyl)-*N*-ethylcyclopropanesulfonamide (251 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (20% acetone/hexane→25% acetone/hexane). White solid.

(*S,S*)-**N1***: 166 mg, 63% yield, 88% ee; (*R,R*)-**N1***: 170 mg, 64% yield, 87% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 3.6 min (major), 8.1 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.26 (m, 5H), 6.95 (d, *J* = 7.6 Hz, 1H), 4.52 (s, 2H), 4.36 – 4.25 (m, 1H), 3.60 – 3.48 (m, 3H), 3.42 – 3.37 (m, 2H), 3.27 (dd, *J* = 14.9, 4.3 Hz, 1H), 2.32 (tt, *J* = 8.1, 4.7 Hz, 1H), 1.77 – 1.61 (m, 4H), 1.57 – 1.52 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.26 – 1.17 (m, 2H), 1.10 – 0.97 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.3, 138.5, 137.6, 133.0 (q, *J* = 32.6 Hz), 128.4, 127.7, 127.57, 127.55, 126.2 (q, *J* = 282.4 Hz), 125.6 (q, *J* = 3.7 Hz), 72.9, 70.0, 49.7, 48.4, 43.0, 32.7, 29.7, 29.6, 22.5, 14.0, 5.3, 5.2.

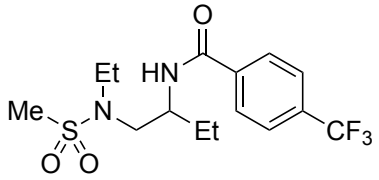
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3354, 2937, 1644, 1545, 1456, 1327, 1167, 1136, 1067, 862, 747, 682 cm^{-1}.

HRMS (LC-MS) *m/z* $(M+H)^+$ calcd for $C_{26}H_{34}F_3N_2O_4S$: 527.2186, found: 527.2191.

$[\alpha]^{24}_D$ = +13 (*c* 1.0, $CHCl_3$); 88% ee from (*S,S*)-**N1***.

m.p.: 116 °C.



***N*-(1-(*N*-Ethylmethylsulfonamido)butan-2-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 57).** The title compound was synthesized according to **GP-10** from *N*-(2-bromobutyl)-*N*-ethylmethanesulfonamide (155 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (20% acetone/hexane→40% acetone/hexane). White solid.

(*S,S*)-**N1***: 134 mg, 73% yield, 89% ee; (*R,R*)-**N1***: 140 mg, 76% yield, 88% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 2.8 min (major), 3.4 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.83 (m, 2H), 7.68 – 7.59 (m, 2H), 6.76 (d, *J* = 7.7 Hz, 1H), 4.24 – 4.12 (m, 1H), 3.42 (dd, *J* = 14.8, 10.6 Hz, 1H), 3.30 (q, *J* = 7.2 Hz, 2H), 3.12 (dd, *J* = 14.9, 4.3 Hz, 1H), 2.81 (s, 3H), 1.70 – 1.48 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 137.6, 133.1 (q, *J* = 32.5 Hz), 127.6, 125.6 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.5 Hz), 49.58, 49.56, 43.1, 39.0, 25.9, 13.9, 10.0.

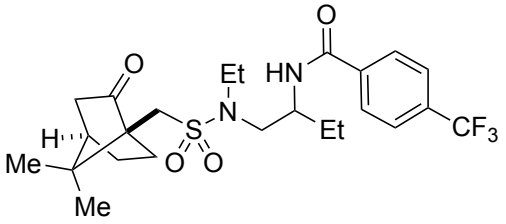
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3304, 2966, 1643, 1544, 1326, 1162, 1136, 1067, 972, 846, 768, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* (M+H)$^+$ calcd for $C_{15}H_{22}F_3N_2O_3S$: 367.1298, found: 367.1310.

$[\alpha]^{24}_D$ = +6.9 (*c* 1.0, $CHCl_3$); 89% ee from (*S,S*)-**N1***.

m.p.: 171 °C.



***N*-(1-((1-((1*S*,4*R*)-7,7-Dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-ethylmethyl) sulfonamido)butan-2-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 58).** The title compound was synthesized according to **GP-10** from *N*-(2-bromobutyl)-1-((1*S*,4*R*)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)-*N*-ethylmethanesulfonamide (237 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol) at –10 °C. The product was purified by flash column chromatography (20% acetone/hexane→25% acetone/hexane). Viscous oil.

(*S,S*)-**N1***: 138 mg, 54% yield, 6:94 dr; (*R,R*)-**N1***: 147 mg, 58% yield, 97:3 dr.

The dr was determined via SFC on a CHIRALPAK ID-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 5.2 min (minor), 5.6 min (major).

Product obtained with (*S,S*)-**N1***:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.65 – 7.58 (m, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 4.25 – 4.12 (m, 1H), 3.46 (dd, *J* = 14.9, 10.8 Hz, 1H), 3.40 – 3.18 (m, 4H), 2.77 (d, *J* = 14.5 Hz, 1H), 2.43 – 2.26 (m, 2H), 2.08 – 1.93 (m, 2H), 1.87 (d, *J* = 18.5 Hz, 1H), 1.71 – 1.50 (m, 3H), 1.37 (ddd, *J* = 13.1, 9.3, 3.9 Hz, 1H), 1.22 – 1.13 (m, 3H), 1.05 (s, 3H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.3, 166.3, 137.6, 133.0 (q, *J* = 32.6 Hz), 127.6, 125.6 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.3 Hz), 58.5, 50.1, 49.6, 48.5, 48.0, 43.4, 42.9, 42.6, 26.9, 26.0, 25.6, 19.9, 19.8, 14.6, 10.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3355, 2966, 1747, 1652, 1538, 1455, 1327, 1131, 1067, 1017, 860, 756 cm^{-1}.

HRMS (LC-MS) *m*/*z* (M+H)$^+$ calcd for $C_{24}H_{34}F_3N_2O_4S$: 503.2186, found: 503.2183.

$[\alpha]^{24}_D$ = +33 (*c* 1.0, $CHCl_3$).

Product obtained with (*R,R*)-**N1***:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.90 (m, 2H), 7.62 – 7.60 (m, 2H), 6.81 (d, *J* = 7.7 Hz, 1H), 4.23 – 4.14 (m, 1H), 3.53 (dd, *J* = 14.9, 11.3 Hz, 1H), 3.41 – 3.21 (m, 3H), 3.12 (dd, *J* = 14.9, 4.1 Hz, 1H), 2.72 (d, *J* = 14.5 Hz, 1H), 2.46 – 2.27 (m, 2H), 2.11 – 1.94 (m, 2H), 1.87 (d, *J* = 18.5 Hz, 1H), 1.69 – 1.52 (m, 3H), 1.41 – 1.35 (m, 1H), 1.18 (t, *J* = 7.2 Hz, 3H), 1.01 (s, 3H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.78 (s, 3H).

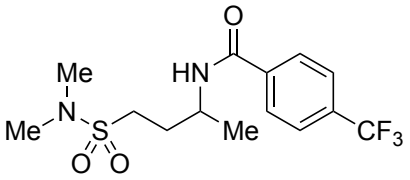
^{13}C NMR (101 MHz, $CDCl_3$) δ 215.4, 166.3, 137.7, 133.0 (q, *J* = 32.6 Hz), 127.6, 125.6 (q, *J* = 3.8 Hz), 123.8 (q, *J* = 272.3 Hz), 58.4, 49.8, 49.4, 48.5, 48.1, 43.1, 42.7, 42.6, 27.0, 26.1, 25.2, 19.9, 19.8, 14.4, 10.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3361, 2966, 1746, 1651, 1538, 1327, 1134, 1067, 1018, 860, 755 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{24}H_{34}F_3N_2O_4S$: 503.2186, found: 503.2183.

$[\alpha]^{24}_D$ = –0.2 (*c* 1.0, $CHCl_3$).



***N*-(4-(*N*,*N*-Dimethylsulfamoyl)butan-2-yl)-4-(trifluoromethyl)benzamide 3-bromo-*N*,*N*-dimethylbutane-1-sulfonamide (Figure 3, entry 59).** The title compound was synthesized according to **GP-13** from 3-bromo-*N*,*N*-dimethylbutane-1-sulfonamide (183 mg, 0.75 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S,S*)-**N1***: 145 mg, 82% yield, 88% ee; (*R,R*)-**N1***: 153 mg, 87% yield, 89% ee.

The ee was determined via SFC on a CHIRALPAK IC-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 4.9 min (minor), 6.5 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 6.68 (d, *J* = 8.3 Hz, 1H), 4.42 – 4.33 (m, 1H), 3.14 (ddd, *J* = 13.8, 9.6, 6.3 Hz, 1H), 3.02 (ddd, *J* = 13.9, 9.6, 5.2 Hz, 1H), 2.90 (s, 6H), 2.26 – 2.07 (m, 2H), 1.39 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 137.5, 133.3 (q, *J* = 32.7 Hz), 127.5, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 45.1, 45.0, 37.5, 29.9, 21.0.

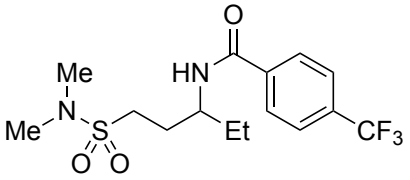
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3309, 2975, 1639, 1543, 1326, 1132, 960, 854, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{14}H_{20}F_3N_2O_3S$: 353.1141, found: 353.1145.

$[\alpha]^{24}_D$ = –14 (*c* 1.0, $CHCl_3$); 88% ee from (*S,S*)-**N1***.

m.p.: 143 °C.



***N*-(1-(*N*,*N*-Dimethylsulfamoyl)pentan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 60).** The title compound was synthesized according to **GP-13** from 3-bromo-*N*,*N*-dimethylpentane-1-sulfonamide (194 mg, 0.75 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (20% acetone/hexane). White solid.

(*S*,*S*)-**N1***: 142 mg, 77% yield, 89% ee; (*R*,*R*)-**N1***: 139 mg, 73% yield, 88% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 3.9 min (major), 6.0 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 8.9 Hz, 1H), 4.29 – 4.14 (m, 1H), 3.15 – 3.09 (m, 1H), 3.05 – 2.97 (m, 1H), 2.89 (s, 6H), 2.28 – 2.22 (m, 1H), 2.11 – 2.03 (m, 1H), 1.82 – 1.65 (m, 3H), 1.05 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 137.5, 133.3 (q, *J* = 32.7 Hz), 127.5, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 50.5, 44.9, 37.4, 28.2, 28.1, 10.4.

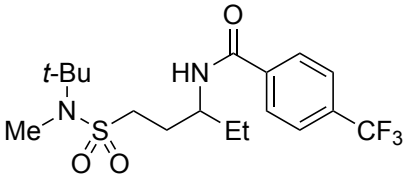
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3313, 2968, 1644, 1538, 1456, 1327, 1171, 1138, 1067, 958, 857, 756 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{15}H_{22}F_3N_2O_3S$: 367.1298, found: 367.1294.

$[\alpha]^{24}_D$ = –6.5 (*c* 1.0, $CHCl_3$); 89% ee from (*S*,*S*)-**N1***.

m.p.: 124 °C.



***N*-(1-(*N*-(*tert*-Butyl)-*N*-methylsulfamoyl)pentan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 61).** The title compound was synthesized according to **GP-13** from 3-bromo-*N*-(*tert*-butyl)-*N*-methylpentane-1-sulfonamide (225 mg, 0.75 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (33% EtOAc/hexane). White solid.

(*S*,*S*)-**N1***: 136 mg, 66% yield, 90% ee; (*R*,*R*)-**N1***: 140 mg, 68% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK AD-3 column (10% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 4.6 min (major), 6.8 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 6.52 (d, *J* = 8.9 Hz, 1H), 4.14 – 3.97 (m, 1H), 3.12 – 3.05 (m, 1H), 3.01 – 2.94 (m, 1H), 2.76 (s, 3H), 2.15 – 2.06 (m, 1H), 1.98 – 1.88 (m, 1H), 1.69 – 1.50 (m, 2H), 1.32 (s, 9H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 137.7, 133.2 (q, *J* = 32.7 Hz), 127.5, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.5 Hz), 58.6, 51.6, 50.5, 32.4, 29.4, 28.5, 28.1, 10.4.

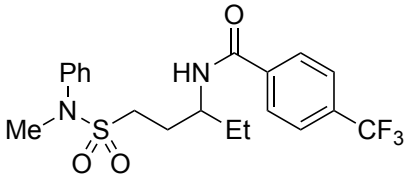
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3323, 2969, 1644, 1544, 1327, 1170, 1132, 1067, 1018, 908, 860, 767 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+Na)^+$ calcd for $C_{18}H_{27}F_3N_2NaO_3S$: 431.1587, found: 431.1584.

$[\alpha]^{24}_D$ = –9.2 (*c* 1.0, $CHCl_3$); 90% ee from (*S,S*)-**N1***.

m.p.: 63 °C.



***N*-(1-(*N*-Methyl-*N*-phenylsulfamoyl)pentan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 62).** The title compound was synthesized according to **GP-13** from 3-bromo-*N*-methyl-*N*-phenylpentane-1-sulfonamide (240 mg, 0.75 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (33% EtOAc/hexane). White solid.

(*S,S*)-**N1***: 114 mg, 53% yield, 90% ee; (*R,R*)-**N1***: 112 mg, 52% yield, 90% ee.

The ee was determined via SFC on a CHIRALPAK ID-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 5.1 min (major), 8.3 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.31 – 7.10 (m, 5H), 6.41 (d, *J* = 8.9 Hz, 1H), 4.09 – 3.91 (m, 1H), 3.21 (s, 3H), 3.13 – 3.06 (m, 1H), 3.01 – 2.94 (m, 1H), 2.13 – 2.05 (m, 1H), 1.96 – 1.86 (m, 1H), 1.63 – 1.45 (m, *J* = 6.7 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 141.1, 137.5, 133.2 (q, *J* = 32.7 Hz), 129.4, 127.53, 127.48, 126.5, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 272.6 Hz), 50.5, 46.1, 38.4, 28.1, 28.0, 10.4.

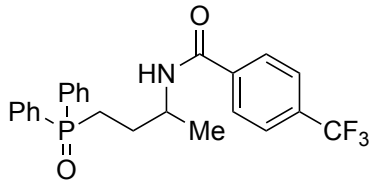
^{19}F NMR (282 MHz, $CDCl_3$) δ –63.0.

FT-IR (film) 3340, 2972, 1644, 1538, 1330, 1170, 1136, 1068, 1017, 896, 857, 768, 701 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{20}H_{24}F_3N_2O_3S$: 429.1454, found: 429.1447.

$[\alpha]^{24}_D$ = –20 (*c* 1.0, $CHCl_3$); 90% ee from (*S,S*)-**N1***.

m.p.: 83 °C.



***N*-(4-(Diphenylphosphoryl)butan-2-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 63).** The title compound was synthesized according to **GP-13** from (3-bromobutyl)

diphenylphosphine oxide (253 mg, 0.75 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (66% EtOAc/CH_2Cl_2). White solid.

(*S,S*)-**N1***: 119 mg, 53% yield, 98% ee; (*R,R*)-**N1***: 128 mg, 58% yield, 98% ee.

The ee was determined via HPLC on a CHIRALPAK AD-H column (30% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 5.2 min (major), 11.4 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 7.7 Hz, 1H), 8.04 (d, *J* = 8.1 Hz, 2H), 7.70 – 7.63 (m, 2H), 7.60 – 7.46 (m, 5H), 7.46 – 7.38 (m, 3H), 7.36 – 7.27 (m, 2H), 4.30 – 4.20 (m, 1H), 2.51 – 2.38 (m, 1H), 2.34 – 2.24 (m, 1H), 2.01 – 1.81 (m, 2H), 1.24 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 137.8, 132.8 (q, *J* = 32.5 Hz), 132.2 (d, *J* = 99.6 Hz), 132.11 (d, *J* = 99.6 Hz), 132.10 (d, *J* = 2.6 Hz), 132.07 (d, *J* = 2.6 Hz), 130.7 (d, *J* = 17.3 Hz), 130.6 (d, *J* = 17.3 Hz), 128.9 (d, *J* = 11.7 Hz), 128.8 (d, *J* = 11.7 Hz), 127.9, 125.3 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 272.5 Hz), 45.9 (d, *J* = 7.6 Hz), 27.8 (d, *J* = 4.1 Hz), 25.7 (d, *J* = 71.3 Hz), 20.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 34.7.

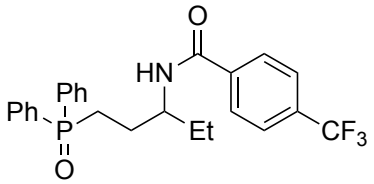
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3264, 2930, 1651, 1554, 1438, 1327, 1170, 1123, 1067, 1018, 862, 755, 682 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{24}H_{24}F_3NO_2P$: 446.1491, found: 446.1494.

$[\alpha]^{24}_D$ = –22 (*c* 1.0, $CHCl_3$); 98% ee from (*S,S*)-**N1***.

m.p.: 115°C.



***N*-(1-(Diphenylphosphoryl)pentan-3-yl)-4-(trifluoromethyl)benzamide (Figure 3, entry 64).** The title compound was synthesized according to **GP-13** from (3-bromopentyl) diphenylphosphine oxide (263 mg, 0.75 mmol) and 4-(trifluoromethyl)benzamide (94.5 mg, 0.50 mmol). The product was purified by flash column chromatography (66% EtOAc/CH_2Cl_2). White solid.

(*S,S*)-**N1***: 120 mg, 52% yield, 95% ee; (*R,R*)-**N1***: 126 mg, 55% yield, 96% ee.

The ee was determined via HPLC on a CHIRALPAK AD-H column (30% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 4.9 min (major), 9.7 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.1 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.72 (m, 4H), 7.65 – 7.59 (m, 3H), 7.56 – 7.51 (m, 3H), 7.43 – 7.41 (m, 2H), 4.30 – 4.16 (m, 1H), 2.59 – 2.51 (m, 1H), 2.46 – 2.34 (m, 1H), 2.12 – 1.99 (m, 2H), 1.84 – 1.69 (m, 2H), 1.01 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 137.8, 132.8 (q, *J* = 33.2 Hz), 132.2 (d, *J* = 94.3 Hz), 132.12 (d, *J* = 94.3 Hz), 132.10 (d, *J* = 2.9 Hz), 132.08 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 9.4 Hz), 130.6 (d, *J* = 9.4

Hz), 128.9 (d, *J* = 7.7 Hz), 128.8 (d, *J* = 7.7 Hz), 127.8, 125.4 (q, *J* = 3.8 Hz), 123.9 (q, *J* = 265.3 Hz), 50.9 (d, *J* = 7.1 Hz), 27.5, 25.9 (d, *J* = 9.0 Hz), 25.5 (d, *J* = 58.1 Hz), 10.5.

^{31}P NMR (162 MHz, $CDCl_3$) δ 34.6.

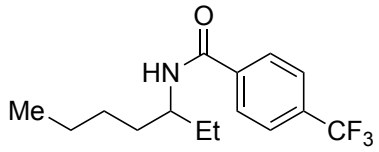
^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3410, 2966, 1652, 1555, 1438, 1327, 1170, 1123, 1068, 1018, 849, 719, 672 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{25}H_{26}F_3NO_2P$: 460.1648, found: 460.1648.

$[\alpha]^{24}_D$ = –25 (*c* 1.0, $CHCl_3$); 95% ee from (*S*,*S*)-**N1***.

m.p.: 109 °C.



***N*-(Heptan-3-yl)-4-(trifluoromethyl)benzamide.** The title compound was synthesized according to **GP-10** from 3-bromoheptane (108 mg, 0.60 mmol) and 4-(trifluoromethyl)benzamide (95 mg, 0.50 mmol). Reaction time: 48 h. The product was purified by flash column chromatography (20% EtOAc/hexane). White solid.

(*S*,*S*)-**N1***: 82 mg, 57% yield, 8% ee; (*R*,*R*)-**N1***: 86 mg, 60% yield, 8% ee.

The ee was determined via SFC on a CHIRALPAK IG-3 column (5% 2-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S*,*S*)-**N1***: 9.0 min (minor), 10.1 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 5.84 (d, *J* = 8.2 Hz, 1H), 4.11 – 4.04 (m, 1H), 1.72 – 1.56 (m, 3H), 1.53 – 1.46 (m, 2H), 1.42 – 1.22 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.90 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.0, 138.4, 133.0 (q, *J* = 32.7 Hz), 127.3, 123.7 (q, *J* = 272.5 Hz), 125.6 (q, *J* = 3.7 Hz), 51.4, 34.5, 28.2, 28.0, 22.7, 14.0, 10.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9.

FT-IR (film) 3302, 2926, 1639, 1328, 1129 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{15}H_{21}F_3NO$: 288.1570, found: 288.1571.

$[\alpha]^{24}_D$ = –1.0 (*c* 0.8, $CHCl_3$); 8% ee from (*S*,*S*)-**N1***.

b.p.: 101 °C.

V. Effect of Reaction Parameters

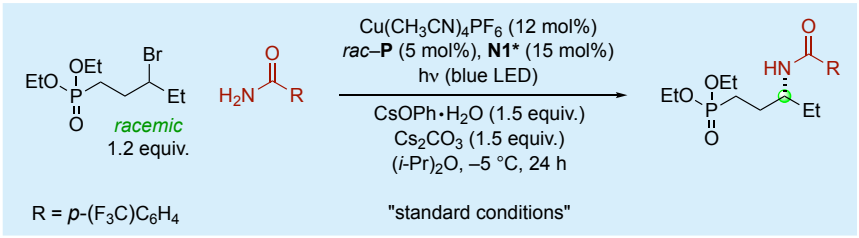
General Procedure 14 (GP-14): In a glovebox, $Cu(CH_3CN)_4PF_6$ (4.5 mg, 0.012 mmol, 12 mol%), racemic diphosphine ligand **P** (5.2 mg, 0.0050 mmol, 5.0 mol%), chiral diamine ligand **N1*** (5.6 mg, 0.015 mmol, 15 mol%), $CsOPh{\cdot}H_2O$ (36.6 mg, 0.15 mmol, 1.5 equiv), and Cs_2CO_3 (48.9 mg, 0.15 mmol, 1.5 equiv) were weighed into a 4 mL vial, followed by the addition of a stir bar. Anhydrous *i*-Pr_2O (3.0 mL) was added via syringe, and the reaction mixture was allowed to stir at room temperature for 30 min. Next, the amide (0.10 mmol) was weighed into the vial, and the suspension was stirred for an additional 5 min, followed by the addition of the γ-bromophosphonate (0.12 mmol, 1.2 equiv) via a microsyringe. The 4 mL vial was sealed with a white polypropylene-lined screw cap, transferred out of the glovebox, placed into a cryocool with a well-stirred isopropanol bath precooled to −5 °C, and fixed upside down with a copper wire holder. The reaction mixture was stirred at −5 °C for 5 min, and then it was irradiated with two PR 440 nm Kessil blue LED lamps, placed ~5 cm away, for 24 h. Next, the reaction was quenched with MeOH, and the mixture was passed through a short pad of silica gel with MeOH as the eluent. The resulting solution was concentrated, and the residue was purified by preparative TLC (10:1 EtOAc/MeOH).

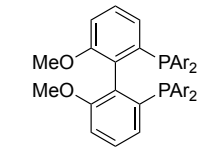
The yield of product was determined via ^{19}F NMR analysis. The ee was determined via HPLC or SFC analysis after purification by preparative TLC.

Notes:

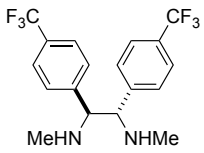
- For reactions that proceed in low yield, the major side products generally are olefins derived from the elimination of HBr.
- We believe that $CsOPh{\bullet}H_2O$ and $CsOPh{\bullet}2H_2O$ are more effective than anhydrous CsOPh due to their superior solubility.
- When the coupling illustrated in Entry 33 of Fig. 3 is conducted in *i*-Pr_2O, somewhat lower yield and ee are observed (75% yield, 83% ee).

Table S1. Effect of reaction parameters. All data are the average of two runs.



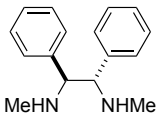


Ar = (3,5-di-*t*-butyl)phenyl
rac–**P**

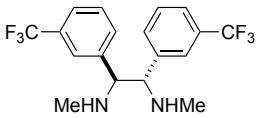


N1*

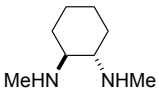
Entry	Change from the "standard conditions"	Yield (%)	ee (%)
1	none	92	93
2	no $Cu(CH_3CN)_4PF_6$	<1	–
3	no *rac*–**P**	<1	–
4	no **N1***	7	0
5	no hν	<1	–
6	no $CsOPh·H_2O$	2	NA
7	no Cs_2CO_3	87	91
8	(*S*)–**P**, instead of *rac*–**P**	88	93
9	(*R*)–**P**, instead of *rac*–**P**	90	93
10	**N2***, instead of **N1***	75	94
11	**L1**, instead of **N1***	75	92
12	**L2**, instead of **N1***	20	81
13	**L3**, instead of **N1***	4	44
14	1.0 equiv of electrophile	74	93
15	1.0 equiv of electrophile, 1.2 equiv of nucleophile	74	93
16	$Cu(CH_3CN)_4PF_6$ (6.0 mol%), *rac*–**P** (2.5 mol%), **N1*** (7.5 mol%)	61	91
17	CuCl, instead of $Cu(CH_3CN)_4PF_6$	88	93
18	10 mol% **N1***	75	92
19	1.2 equiv of $CsOPh·H_2O$	70	91
20	CsOPh, instead of $CsOPh·H_2O$	4	84
21	$CsOPh·2H_2O$, instead of $CsOPh·H_2O$	85	92
22	$KOPh·H_2O$, instead of $CsOPh·H_2O$	55	92
23	NaOPh, instead of $CsOPh·H_2O$	5	56
24	Et_2O, instead of $(i\text{-Pr})_2O$	7	83
25	2-Me-THF, instead of $(i\text{-Pr})_2O$	6	78
26	–20 °C	82	96
27	r.t.	<1	–
28	1.0 equiv H_2O added	88	92
29	0.10 mL air added	86	92



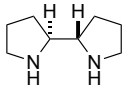
N2*



L1



L2

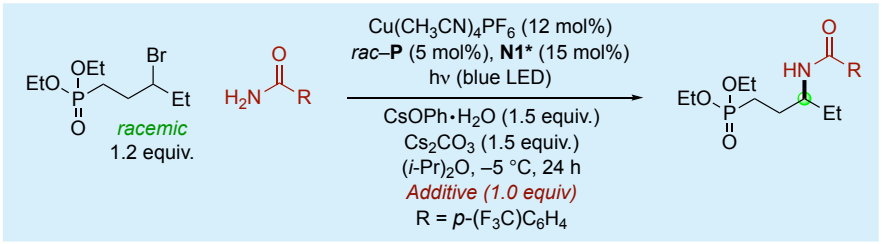


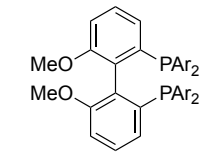
L3

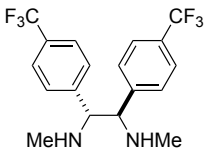
VI. Functional-Group Compatibility

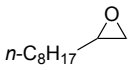
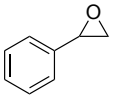
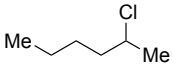
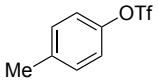
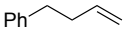
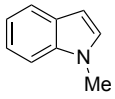
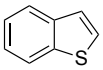
GP-14 was followed in the presence of 1.0 equiv of an additive. The yield of product was determined via ^{19}F NMR analysis. The ee was determined via SFC analysis after purification by preparative TLC. The recovery of the additive was determined via GC analysis using dodecane as an internal standard.

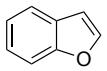
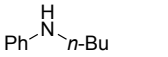
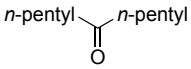
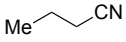
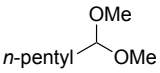
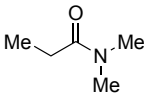
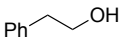
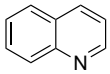
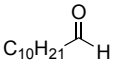
Table S2. Effect of additives. All data are the average of two runs.







Entry	Additive	Recovery of additive (%)	Yield (%)	ee (%)
1		>95	90	93
2		>95	84	93
3		>95	86	93
4		>95	88	93
5		>95	89	93
6		>95	84	93
7		>95	86	93
8		>95	89	93
9		>95	89	93
10		>95	88	93
11		>95	88	93

Entry	Additive	Recovery of additive (%)	Yield (%)	ee (%)
12		>95	81	93
13		>95	85	93
14		>95	80	92
15		>95	85	92
16		>95	88	92
17		>95	83	91
18		>95	77	93
19	PhOTs	>95	79	90
20		>95	72	89
21		74	75	93
22	EtN(*i*-Pr)$_2$	50	86	93

VII. Transformations of the Coupling Products

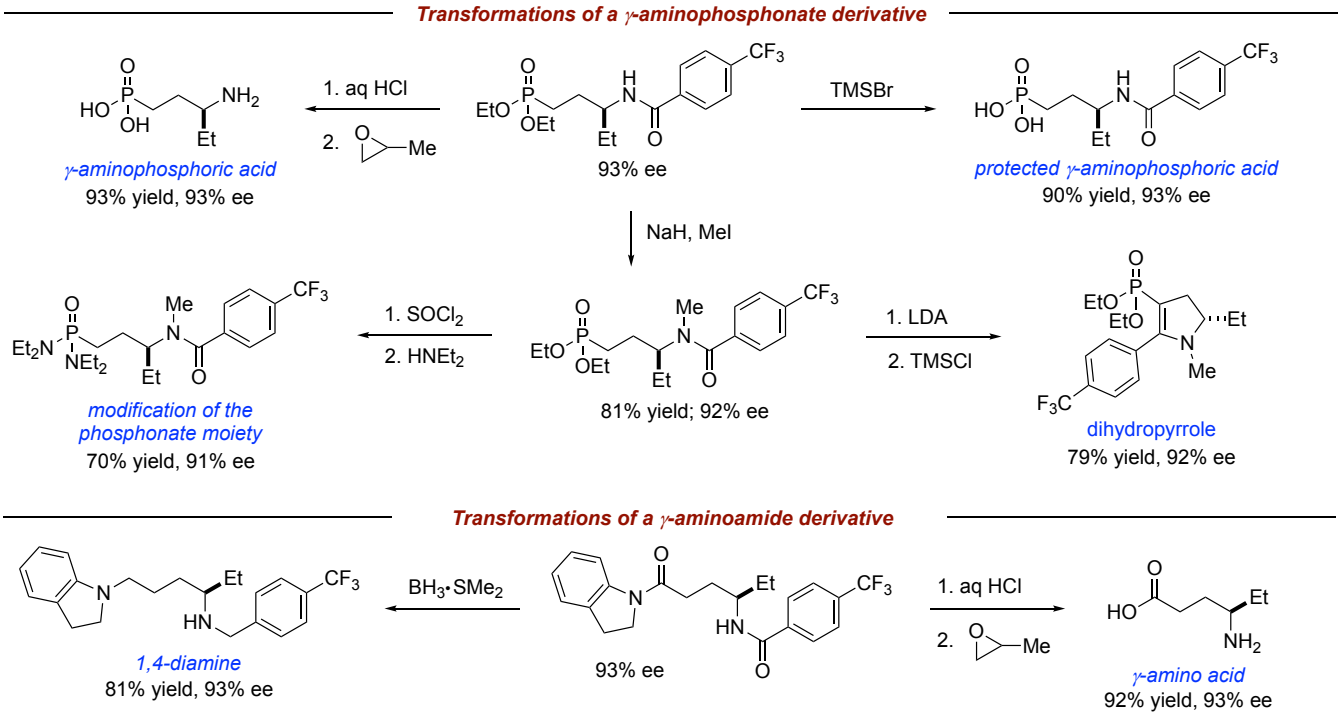
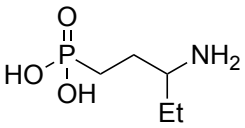


Figure S1. Transformations of the coupling products. All data represent the average of two experiments. The percent yield represents purified product.



(3-Aminopentyl)phosphonic acid. A solution of diethyl (3-(4-(trifluoromethyl) benzamido)pentyl)phosphonate (79 mg, 0.20 mmol) in aqueous HCl (12 N, 2.0 mL) was heated at reflux for 24 h. The resulting suspension was then filtered. The solid was washed with water (2.0 mL), and the combined filtrate was concentrated by rotary evaporation. The residue was then dissolved in EtOH (1.0 mL), followed by the dropwise addition of propylene oxide (1.5 mL) at room temperature. The mixture was stirred at room temperature for 2 h. The resulting precipitate was then collected and dried under vacuum to afford the title product. White solid.

(*S,S*)-**N1***: 30.2 mg, 90% yield, 93% ee; (*R,R*)-**N1***: 31.8 mg, 95% yield, 93% ee.

In order to determine the ee, (3-aminopentyl)phosphonic acid was converted to dimethyl (3-benzamidopentyl)phosphonate by first reacting it with benzoyl chloride in the presence of sodium carbonate to generate (3-benzamidopentyl)phosphonic acid, which was then reacted with oxalyl chloride and then with MeOH. The ee of dimethyl (3-benzamidopentyl) phosphonate was determined via SFC on a CHIRALPAK IG-3 column (20% *i*-PrOH in

supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 5.6 min (major), 6.1 min (minor).

^{1}H NMR (500 MHz, D_2O) δ 3.14 (p, *J* = 6.4 Hz, 1H), 1.81 – 1.70 (m, 2H), 1.66 – 1.43 (m, 4H), 0.86 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, D_2O) δ 53.5 (d, *J* = 16.7 Hz), 25.8 (d, *J* = 3.9 Hz), 24.5, 23.5 (d, *J* = 134.2 Hz), 8.4.

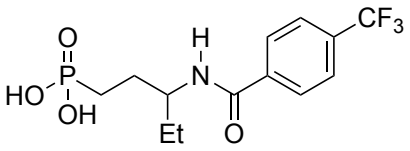
^{31}P NMR (121 MHz, D_2O) δ 26.3.

FT-IR (film) 3400, 2918, 2358, 1643, 1538, 1132, 1049, 891, 720 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_5H_{15}NO_3P$: 168.0784, found: 168.0800.

$[\alpha]^{24}_D$ = –1.2 (*c* 1.0, MeOH); 93% ee from (*S,S*)-**N1***.

m.p.: 245-246 °C.



(3-(4-(Trifluoromethyl)benzamido)pentyl)phosphonic acid. Me_3SiBr (153 mg, 1.0 mmol) was added dropwise to a 0 °C solution of diethyl (3-(4-(trifluoromethyl)benzamido)pentyl)-phosphonate (79 mg, 0.20 mmol) in anhydrous CH_2Cl_2 (1.0 mL). The resulting solution was allowed to warm to room temperature and stir for 5 h. Next, the solution was concentrated, water (1.0 mL) was added to the residue, and the suspension was stirred for 20 min. The resulting white solid was collected, washed with cold water (1 mL), and dried to afford the desired product.

(*S,S*)-**N1***: 60 mg, 88% yield, 93% ee; (*R,R*)-**N1***: 62 mg, 91% yield, 93% ee.

In order to determine the ee, (3-(4-(trifluoromethyl)benzamido)pentyl)phosphonic acid was converted to dimethyl (3-(4-(trifluoromethyl)benzamido)pentyl)phosphonate by treating with oxalyl chloride and subsequently with MeOH. The ee of dimethyl (3-(4-(trifluoromethyl) benzamido)pentyl)phosphonate was determined via SFC on a CHIRALPAK IG-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 5.6 min (major), 6.1 min (minor).

^{1}H NMR (400 MHz, CD_3OD) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 7.9 Hz, 2H), 4.04 – 3.98 (m, 1H), 2.00 – 1.89 (m, 1H), 1.84 – 1.51 (m, 5H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, CD_3OD) δ 167.7, 138.3, 132.6 (q, *J* = 32.5 Hz), 127.7, 125.1 (q, *J* = 3.7 Hz), 123.9 (q, *J* = 271.7 Hz), 52.3 (d, *J* = 17.8 Hz), 27.6 (d, *J* = 4.1 Hz), 27.1, 23.6 (d, *J* = 139.0 Hz), 9.6.

^{31}P NMR (162 MHz, CD_3OD) δ 29.6.

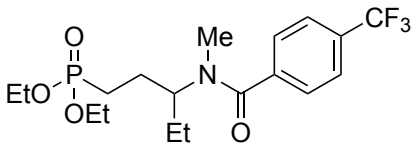
^{19}F NMR (282 MHz, CD_3OD) δ –64.5.

FT-IR (film) 3322, 2967, 2359, 1636, 1539, 1328, 1131, 1068, 1017, 957, 856, 681 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{13}H_{18}F_3NO_4P$: 340.0920, found: 340.0926.

$[\alpha]^{24}_D$ = +6.9 (*c* 0.50, MeOH); 93% ee from (*S,S*)-**N1***.

m.p.: 174 °C.



Diethyl (3-(*N*-methyl-4-(trifluoromethyl)benzamido)pentyl)phosphonate. To a 0 °C solution of diethyl (3-(4-(trifluoromethyl)benzamido)pentyl)phosphonate (395 mg, 1.0 mmol) in anhydrous THF (8.0 mL) was added NaH (60 wt% in mineral oil, 60.0 mg, 1.5 mmol) in small portions. The resulting mixture was allowed to warm to room temperature and stir for 30 min. Iodomethane (284 mg, 2.0 mmol) was added dropwise at room temperature, and the resulting mixture was stirred for 12 h. After the solution was concentrated, the residue was purified by flash column chromatography on silica gel (EtOAc→5% MeOH/ EtOAc) to afford the desired product. Colorless oil.

(*S,S*)-**N1***: 336 mg, 82% yield, 92% ee; (*R,R*)-**N1***: 323 mg, 79% yield, 92% ee.

The ee was determined via SFC on a CHIRALPAK IG-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 9.4 min (major), 10.0 min (minor).

^{1}H NMR (500 MHz, $CDCl_3$), two rotamers, δ 7.70 (dd, *J* = 8.2, 4.0 Hz, 2H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 4.71 (tt, *J* = 10.1, 5.2 Hz, 0.5 H) and 3.46 (tt, *J* = 9.3, 5.4 Hz, 0.5 H), 4.22 – 4.02 (m, 4H), 2.94 (s, 1.5H) and 2.73 (s, 1.5H), 1.98 – 1.45 (m, 6H), 1.40 – 1.24 (m, 6H), 1.01 (t, *J* = 7.3 Hz, 1.5H) and 0.89 (t, *J* = 7.4 Hz, 1.5H).

^{13}C NMR (101 MHz, $CDCl_3$), two rotamers, δ 171.4 and 171.5, 140.6 and 140.5, 131.4 (q, *J* = 32.7 Hz) and 131.2 (q, *J* = 32.7 Hz), 127.2 and 127.0, 125.7 (q, *J* = 3.8 Hz) and 125.6 (q, *J* = 3.8 Hz), 123.72 (q, *J* = 272.4 Hz) and 123.68 (q, *J* = 272.4 Hz), 61.8 – 61.6 (m), 60.2 and 60.0, 54.9 and 54.7, 30.5, 26.0, 25.71, 25.66, 24.8, 24.63 and 24.59, 22.8 (d, *J* = 143.2 Hz) and 22.7 (d, *J* = 142.6 Hz), 16.5 (d, *J* = 5.9 Hz) and 16.4 (d, *J* = 6.1 Hz), 10.8 and 10.7.

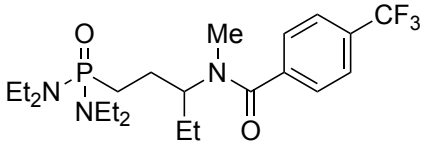
^{31}P NMR (162 MHz, $CDCl_3$), two rotamers, δ 31.6 and 30.5.

^{19}F NMR (282 MHz, $CDCl_3$), two rotamers, δ –62.91 and –62.92.

FT-IR (film) 3477, 2968, 1633, 1520, 1446, 1403, 1327, 1243, 1168, 1123, 1032, 968, 848, 613 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{18}H_{28}F_3NO_4P$: 410.1703, found: 410.1706.

$[\alpha]^{24}_D$ = –29 (*c* 1.0, $CHCl_3$); 92% ee from (*R,R*)-**N1***.



***N*-(1-(Bis(diethylamino)phosphoryl)pentan-3-yl)-*N*-methyl-4-(trifluoromethyl) benzamide.** Diethyl (3-(*N*-methyl-4-(trifluoromethyl)benzamido)pentyl)phosphonate (82 mg, 0.20 mmol) was dissolved in $SOCl_2$ (0.5 mL). To the solution was added one drop of DMF, and the resulting mixture was heated at reflux for 6 h. After the mixture was cooled and concentrated, the residue was dried under high vacuum for 1 h. The residue was then

dissolved in anhydrous CH_2Cl_2 (1.0 mL), and $HNEt_2$ (73 mg, 1.0 mmol) was added dropwise at 0 °C. The resulting mixture was allowed to warm to room temperature and stir for 6 h. Next, the mixture was concentrated by rotary evaporation, and the residue was purified by flash column chromatography on silica gel (EtOAc→5% MeOH/EtOAc) to afford the desired product. Colorless oil.

(*S,S*)-**N1***: 64 mg, 69% yield, 91% ee; (*R,R*)-**N1***: 65 mg, 71% yield, 91% ee.

The ee was determined via HPLC on a CHIRALPAK IA-H column (10% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 10.3 min (minor), 11.9 min (major).

^{1}H NMR (400 MHz, $CDCl_3$), two rotamers, δ 7.60 (t, *J* = 8.0 Hz, 2H), 7.38 (dd, *J* = 19.0, 7.9 Hz, 2H), 4.64 – 4.57 (m, 0.5H) and 3.40 – 3.32 (m, 0.5H), 3.07 – 2.87 (m, 8H), 2.86 (s, 1.5H) and 2.65 (s, 1.5H), 1.82 – 1.61 (m, 4H), 1.59 – 1.43 (m, 3H), 1.09 – 0.96 (m, 12H), 0.90 (t, *J* = 7.4 Hz, 1.5H) and 0.82 (t, *J* = 7.4 Hz, 1.5H).

^{13}C NMR (101 MHz, $CDCl_3$), two rotamers, δ 171.3 and 171.2, 140.8 and 140.7, 131.4 (q, *J* = 32.7 Hz) and 131.3 (q, *J* = 32.7 Hz), 127.2 and 127.0, 125.7 (q, *J* = 3.7 Hz) and 125.6 (q, *J* = 3.7 Hz), 123.74 (q, *J* = 272.3 Hz) and 123.66 (q, *J* = 272.4 Hz), 60.9 and 60.7, 55.4 and 55.2, 38.7 – 38.6 (m), 30.6 and 29.7, 26.2 and 25.8, 25.78 and 25.76, 25.0, 24.70 and 24.67, 23.5 (d, *J* = 116.2 Hz) and 23.4 (d, *J* = 116.4 Hz), 14.4 (d, *J* = 2.3 Hz) and 14.3 (d, *J* = 2.3 Hz), 10.9 and 10.8.

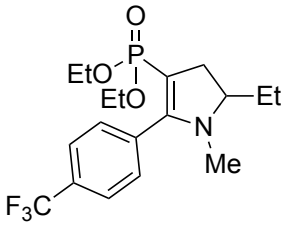
^{31}P NMR (162 MHz, $CDCl_3$), two rotamers, δ 36.63 and 35.58.

^{19}F NMR (282 MHz, $CDCl_3$), two rotamers, δ –62.90 and –62.91.

FT-IR (film) 3429, 2968, 2362, 1633, 1456, 1384, 1326, 1208, 1170, 1128, 1068, 1019, 945, 789 701 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{22}H_{38}F_3N_3O_2P$: 464.2648, found: 464.2642.

$[\alpha]^{24}_D$ = –15 (*c* 1.0, $CHCl_3$); 91% ee from (*R,R*)-**N1***.



Diethyl (5-ethyl-1-methyl-2-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrrol-3-yl)phosphonate. LDA (Sigma-Aldrich, 2.0 M, 0.22 mL, 0.44 mmol) was added dropwise to a –78 °C solution of diethyl (3-(*N*-methyl-4-(trifluoromethyl)benzamido) pentyl)phosphonate (82 mg, 0.20 mmol) in THF (1.0 mL). The mixture was stirred at –78 °C for 20 min, and then TMSCl (23.9 mg, 0.22 mmol) was added dropwise. The resulting mixture was stirred at –78 °C for 15 min, and then it was allowed to warm to room temperature. Water (0.10 mL) was added to quench the reaction, and the mixture was concentrated. The residue was purified by flash column chromatography on silica gel (EtOAc) to afford the desired product. Colorless oil.

(*S,S*)-**N1***: 60 mg, 77% yield, 91% ee; (*R,R*)-**N1***: 63 mg, 81% yield, 92% ee.

The ee was determined via HPLC on a CHIRALPAK AD-H column (2.0% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S,S*)-**N1***: 9.8 min (minor), 11.4 min (major).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 3.88 – 3.65 (m, 4H), 3.38 – 3.30 (m, 1H), 2.92 (ddd, *J* = 14.9, 10.7, 2.5 Hz, 1H), 2.44 (ddd, *J* = 15.0, 10.9, 3.1 Hz, 1H), 2.36 (s, 3H), 1.80 – 1.70 (m, 1H), 1.59 – 1.44 (m, 1H), 1.06 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 23.4 Hz), 136.3, 130.9 (q, *J* = 32.4 Hz), 129.4, 124.9 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 272.2 Hz), 92.3 (d, *J* = 221.8 Hz), 67.4 (d, *J* = 11.1 Hz), 60.9 (d, *J* = 10.2 Hz), 60.8 (d, *J* = 10.2 Hz), 36.2 (d, *J* = 9.6 Hz), 34.9, 26.1, 16.2 (d, *J* = 7.3 Hz), 16.1 (d, *J* = 7.3 Hz), 9.3.

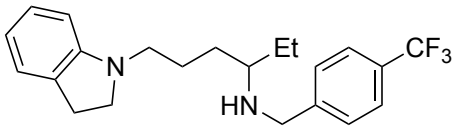
^{31}P NMR (162 MHz, $CDCl_3$) δ 19.8.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.8.

FT-IR (film) 3421, 2983, 1651, 1455, 1326, 1224, 1127, 1032, 965, 852, 802, 748 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{18}H_{26}F_3NO_3P$: 392.1597, found: 392.1592.

$[\alpha]^{24}_D$ = +12 (*c* 1.0, $CHCl_3$); 92% ee from (*R,R*)-**N1***.



6-(Indolin-1-yl)-*N*-(4-(trifluoromethyl)benzyl)hexan-3-amine. To a 0 °C solution of *N*-(6-(indolin-1-yl)-6-oxohexan-3-yl)-4-(trifluoromethyl)benzamide (80.9 mg, 0.20 mmol) in THF (2.0 mL) was added borane-SMe_2 (2.0 M in THF, 0.25 mL, 0.50 mmol). The reaction mixture was allowed to warm to room temperature, and then it was heated at reflux for 12 h. The reaction was quenched with aqueous NaOH (1.0 M, 1.0 mL). The reaction mixture was extracted with Et_2O (3 x 10 mL), and the organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated by rotatory evaporation. The residue was purified by flash column chromatography on silica gel (10% EtOAc/hexane) to afford the desired product. Colorless oil.

(*S,S*)-**N2***: 60 mg, 78% yield, 93% ee; (*R,R*)-**N2***: 63 mg, 83% yield, 92% ee.

The ee was determined via HPLC on a CHIRALPAK AS-H column (1.0% *i*-PrOH in hexanes, 1.0 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 4.9 min (minor), 6.0 min (major).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.16 – 7.08 (m, 2H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.8 Hz, 1H), 3.94 – 3.84 (m, 2H), 3.39 (t, *J* = 8.3 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 8.3 Hz, 2H), 2.62 (p, *J* = 5.9 Hz, 1H), 1.74 – 1.69 (m, 2H), 1.66 – 1.53 (m, 4H), 0.99 (t, *J* = 7.4 Hz, 3H).

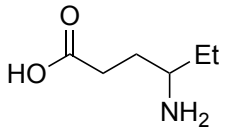
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 145.2, 130.0, 129.1 (q, *J* = 32.3 Hz), 128.3, 127.3, 125.3 (q, *J* = 3.8 Hz), 124.4, 124.3 (q, J = 271.8 Hz), 117.4, 106.9, 57.9, 53.2, 50.6, 49.6, 31.0, 28.6, 26.3, 23.5, 9.80

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.4.

FT-IR (film) 2932, 1607, 1488, 1326, 1162, 1123, 1066, 1018, 826, 746 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{22}H_{28}F_3N_2$: 377.2199, found: 377.2200.

$[\alpha]^{24}_D$ = +1.7 (*c* 1.0, $CHCl_3$); 93% ee from (*S,S*)-**N2***.



4-Aminohexanoic acid. A suspension of *N*-(6-(indolin-1-yl)-6-oxohexan-3-yl)-4-(trifluoromethyl)benzamide (0.20 mmol, 81 mg) in aqueous HCl (12 N, 3.0 mL) in a sealed 8 mL vial was heated to 110 °C and stirred for 18 h. After the reaction was complete, the suspension was cooled and filtered. The solid was washed with water (1.0 mL), and the filtrate was concentrated. The residue was dissolved in EtOH (0.50 mL), and propylene oxide (2.0 mL) was added dropwise at room temperature. The resulting suspension was stirred at room temperature for 1 h. The white solid was collected, washed with Et_2O (1.0 mL), and dried to give the desired product. White solid.

(*S,S*)-**N2***: 25 mg, 95% yield, 93% ee; (*R,R*)-**N2***: 23 mg, 89% yield, 92% ee.

In order to determine the ee, 4-aminohexanoic acid was converted to 4-benzamidohexanoic acid by reacting with benzoyl chloride in the presence of sodium carbonate. The ee of 4-benzamidohexanoic acid was determined via SFC on a CHIRALPAK ID-3 column (20% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for compound obtained using (*S,S*)-**N2***: 4.2 min (major), 4.9 min (minor).

^{1}H NMR (500 MHz, CD_3OD) δ 3.19 (p, *J* = 6.3 Hz, 1H), 2.56 – 2.44 (m, 4H), 1.99 – 1.87 (m, 2H), 1.77 – 1.70 (m, 2H), 1.08 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, CD_3OD) δ 177.6, 53.1, 31.9, 27.6, 25.6, 8.5.

FT-IR (film) 3418, 2947, 1542, 1416, 1111, 693 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_6H_{14}NO_2$: 132.1019, found: 377.1021.

$[\alpha]^{24}_D$ = –17 (*c* 1.0, MeOH); 92% ee from (*R,R*)-**N2***.

VIII. Assignment of Absolute Configuration

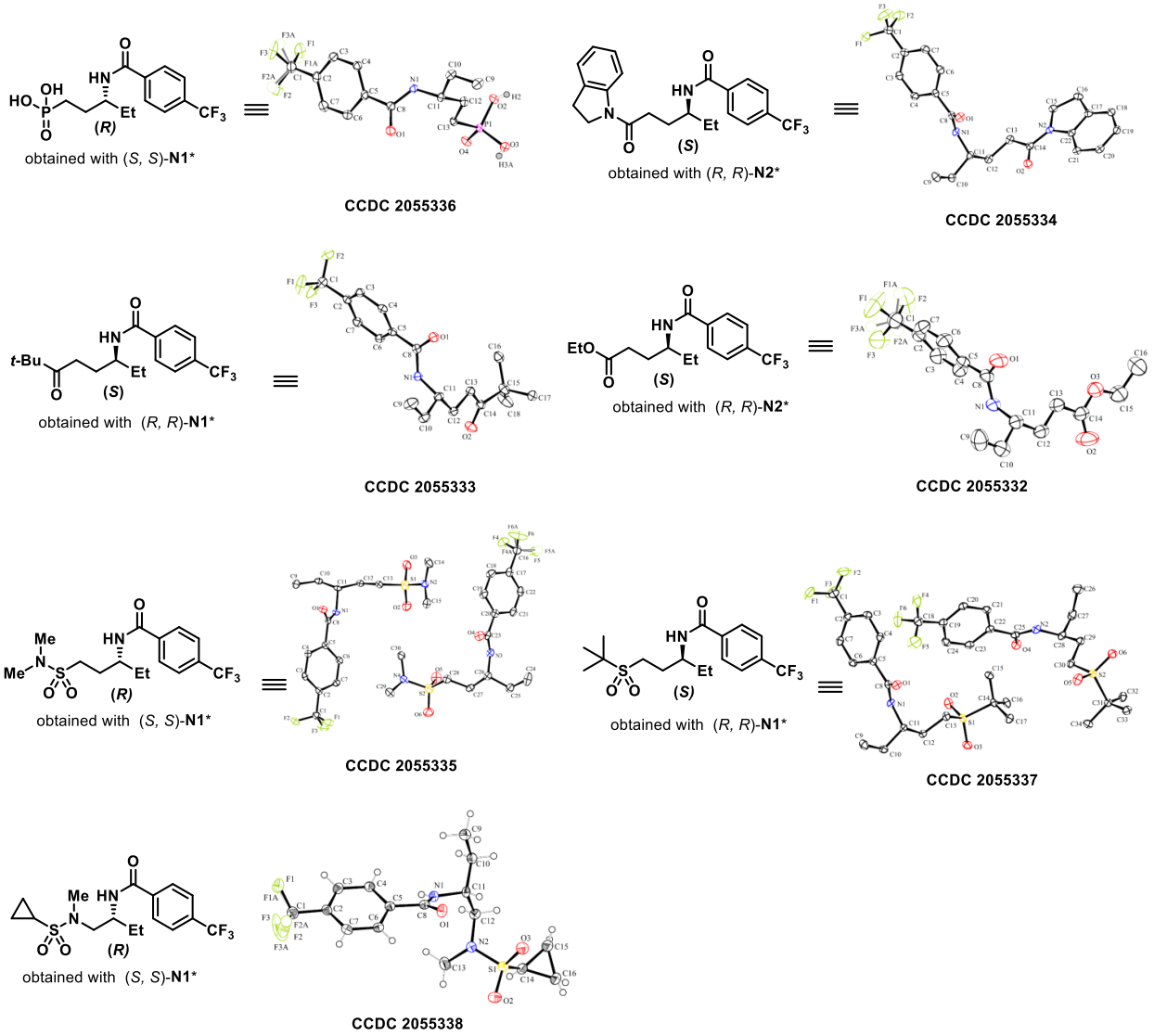
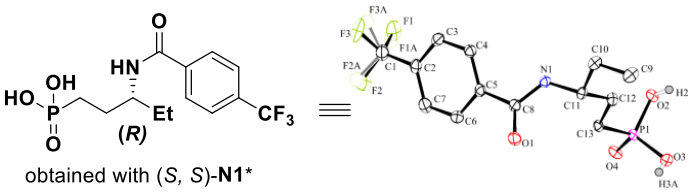


Figure S2. Overview of X-ray crystal structures of the products, with thermal ellipsoids at the 50% probability level.

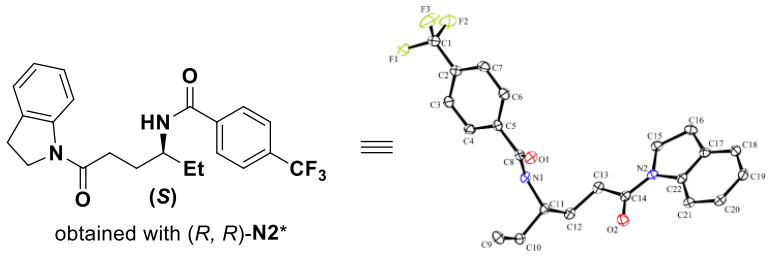


Thermal ellipsoid plot at 50% probability level. C-H and N-H hydrogen atoms are not shown for clarity. The O-H hydrogen atoms were refined isotropically on calculated positions by using a riding model. The N-H hydrogen atom was found in the residual density map and refined isotropically. The disordered CF_3 group was refined with a population of 0.78058 on the main domain using restraints (RIGU, SIMU, SAME).

Data collection and structure refinement

Identification code	v20088
Chemical formula	$C_{13}H_{17}F_3NO_4P$
Formula weight	339.24 g/mol
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal size	0.110 x 0.126 x 0.260 mm
Crystal habit	clear colourless block
Crystal system	monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 5.1814(2) Å α = 90° b = 7.6041(3) Å β = 91.6990(10)° c = 19.2545(8) Å γ = 90°
Volume	758.29(5) $Å^3$
Z	2
Density (calculated)	1.486 g/cm^3
Absorption coefficient	2.095 mm^{-1}
F(000)	352
Theta range for data collection	2.30 to 66.59°
Index ranges	-6<=h<=6, -9<=k<=9, -22<=l<=22
Reflections collected	16194
Independent reflections	2612 [R(int) = 0.0360]
Coverage of independent reflections	99.8%

Absorption correction	Multi-Scan
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2612 / 115 / 234
Goodness-of-fit on F^2	1.136
Final R indices	2586 data; $I>2\sigma(I)$ R1 = 0.0244, wR2 = 0.0628
	all data R1 = 0.0246, wR2 = 0.0629
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0212P)^2+0.3358P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.061(7)
Largest diff. peak and hole	0.268 and -0.261 eÅ^{-3}
R.M.S. deviation from mean	0.045 eÅ^{-3}

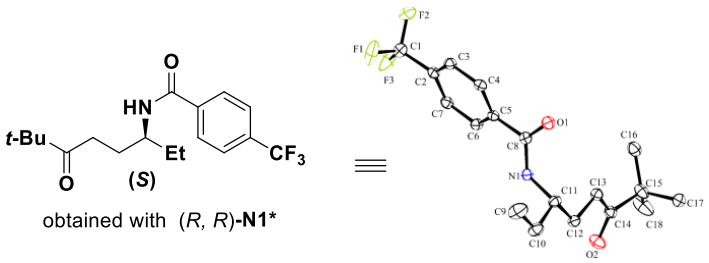


Thermal ellipsoid plot at 50% probability level. Hydrogen atoms are not shown for clarity. The N-H hydrogen atom was found in the residual density map and refined isotropically.

Data collection and structure refinement

Identification code	v20085	
Chemical formula	$C_{22}H_{23}F_3N_2O_2$	
Formula weight	404.42 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.066 x 0.164 x 0.241 mm	
Crystal habit	clear colourless plate	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 5.2266(5) Å	α = 90°
	b = 12.1489(11) Å	β = 90°
	c = 29.908(3) Å	γ = 90°
Volume	1899.1(3) $Å^3$	
Z	4	
Density (calculated)	1.414 g/cm^3	
Absorption coefficient	0.935 mm^{-1}	
F(000)	848	
Theta range for data collection	2.96 to 69.98°	
Index ranges	-6<=h<=6, -14<=k<=14, -36<=l<=36	
Reflections collected	42262	
Independent reflections	3619 [R(int) = 0.0356]	
Coverage of independent reflections	100.0%	
Absorption correction	Multi-Scan	

Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3619 / 0 / 267	
Goodness-of-fit on F^2	1.056	
Δ/σ_{max}	0.001	
Final R indices	3602 data; $I>2\sigma(I)$	R1 = 0.0237, wR2 = 0.0607
	all data	R1 = 0.0239, wR2 = 0.0609
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0307P)^2+0.4182P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.06(2)	
Largest diff. peak and hole	0.184 and -0.179 eÅ^{-3}	
R.M.S. deviation from mean	0.032 eÅ^{-3}	

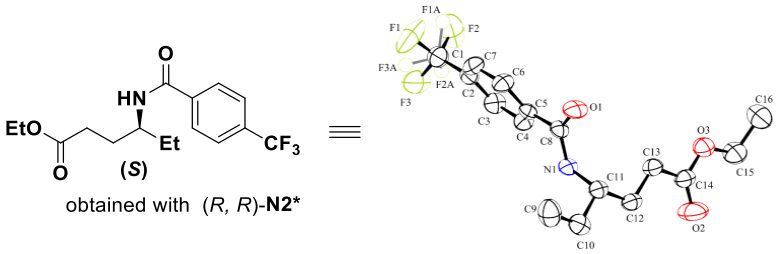


Thermal ellipsoid plot at 50% probability level. Hydrogen atoms are not shown for clarity. The N-H hydrogen atom was found in the residual density map and refined isotropically.

Data collection and structure refinement

Identification code	v20082
Chemical formula	$C_{18}H_{24}F_3NO_2$
Formula weight	343.38 g/mol
Temperature	101(2) K
Wavelength	1.54178 Å
Crystal size	0.054 x 0.238 x 0.281 mm
Crystal habit	clear colourless plate
Crystal system	monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 11.1339(4) Å α = 90° b = 5.3585(2) Å β = 109.693(2)° c = 16.0121(6) Å γ = 90°
Volume	899.42(6) $Å^3$
Z	2
Density (calculated)	1.268 g/cm^3
Absorption coefficient	0.869 mm^{-1}
F(000)	364
Theta range for data collection	2.93 to 66.56°
Index ranges	-13<=h<=13, -6<=k<=6, -19<=l<=18
Reflections collected	22038
Independent reflections	3137 [R(int) = 0.0376]
Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9550 and 0.7920

Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3137 / 1 / 225	
Goodness-of-fit on F^2	1.036	
Final R indices	3047 data; $I>2\sigma(I)$	R1 = 0.0280, wR2 = 0.0710
	all data	R1 = 0.0291, wR2 = 0.0718
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0379P)^2+0.2172P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.03(5)	
Largest diff. peak and hole	0.222 and -0.196 eÅ^{-3}	
R.M.S. deviation from mean	0.031 eÅ^{-3}	

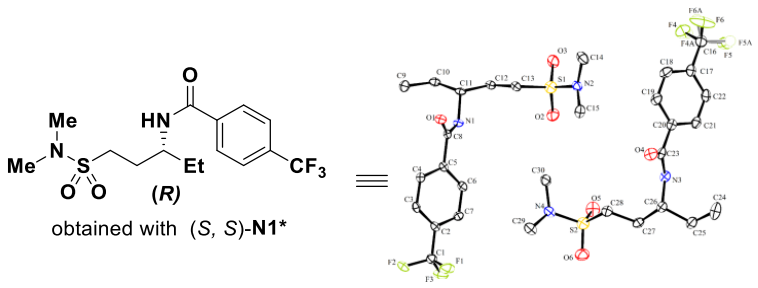


Thermal ellipsoid plot at 50% probability level. Hydrogen atoms are not shown for clarity. The N-H hydrogen atom was found in the residual density map and refined isotropically. The disordered CF_3 group was refined with a population of 0.72696 on the main domain using restraints (SIMU, SAME).

Data collection and structure refinement

Identification code	V20081
Chemical formula	$C_{16}H_{20}F_3NO_3$
Formula weight	331.33 g/mol
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal size	0.063 x 0.066 x 0.322 mm
Crystal habit	clear colourless prism
Crystal system	orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 5.06860(10) Å α = 90°
	b = 15.4695(5) Å β = 90°
	c = 21.3263(7) Å γ = 90°
Volume	1672.17(8) $Å^3$
Z	4
Density (calculated)	1.316 g/cm^3
Absorption coefficient	0.964 mm^{-1}
F(000)	696
Theta range for data collection	3.53 to 66.58°
Index ranges	-6<=h<=5, -18<=k<=18, -25<=l<=25
Reflections collected	24159
Independent reflections	2928 [R(int) = 0.0602]
Coverage of independent reflections	99.9%

Absorption correction	Multi-Scan	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2928 / 78 / 242	
Goodness-of-fit on F^2	1.095	
Δ/σ_{max}	0.004	
Final R indices	2634 data; $I>2\sigma(I)$	R1 = 0.0371, wR2 = 0.0894
	all data	R1 = 0.0424, wR2 = 0.0918
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0384P)^2+0.2674P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.07(9)	
Largest diff. peak and hole	0.156 and -0.143 $eÅ^{-3}$	
R.M.S. deviation from mean	0.030 $eÅ^{-3}$	



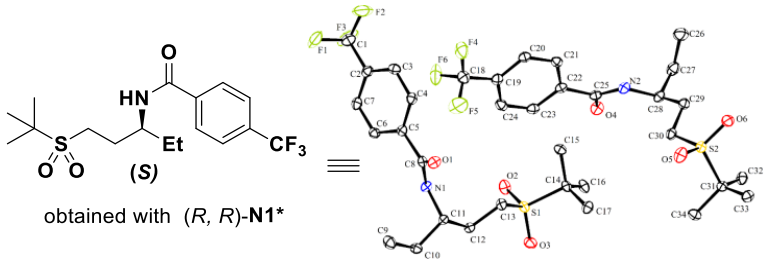
Thermal ellipsoid plot at 50% probability level. The asymmetric unit contains two molecules. Hydrogen atoms are not shown for clarity. The N-H hydrogen atoms were found in the residual density map and refined isotropically. The disordered CF_3 group was refined with a population of 0.57706 on the main domain using restraints (SIMU, SAME).

Data collection and structure refinement

Identification code	v20087	
Chemical formula	$C_{15}H_{21}F_3N_2O_3S$	
Formula weight	366.40 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.048 x 0.124 x 0.287 mm	
Crystal habit	clear colourless plate	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 18.3753(7) Å	$\alpha = 90°$
	b = 5.1195(2) Å	$\beta = 109.865(2)°$
	c = 19.3012(8) Å	$\gamma = 90°$
Volume	1707.67(12) $Å^3$	
Z	4	
Density (calculated)	1.425 g/cm^3	
Absorption coefficient	2.128 mm^{-1}	
F(000)	768	

Theta range for data collection	2.43 to 66.59°
Index ranges	-21<=h<=21, -5<=k<=6, -22<=l<=22
Reflections collected	27789
Independent reflections	5887 [R(int) = 0.0459]
Coverage of independent	98.8%

reflections		
Absorption correction	Multi-Scan	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5887 / 79 / 475	
Goodness-of-fit on F^2	1.058	
Δ/σ_{max}	0.001	
Final R indices	5608 data; $I>2\sigma(I)$	R1 = 0.0282, wR2 = 0.0684
	all data	R1 = 0.0301, wR2 = 0.0691
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0306P)^2+0.3163P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.044(6)	
Largest diff. peak and hole	0.270 and -0.252 $eÅ^{-3}$	
R.M.S. deviation from mean	0.038 $eÅ^{-3}$	

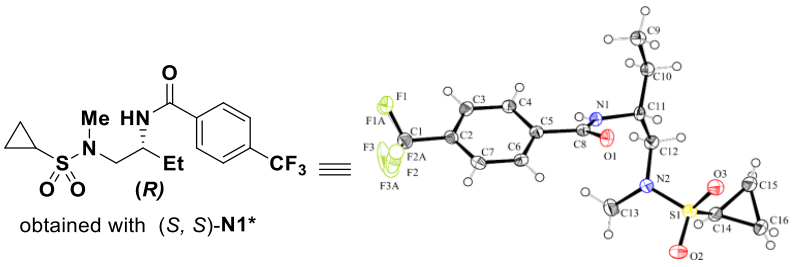


Thermal ellipsoid plot at 50% probability level. The asymmetric unit contains two molecules. Hydrogen atoms are not shown for clarity. The N-H hydrogen atoms were found in the residual density map and refined isotropically.

Data collection and structure refinement

Identification code	v20095
Chemical formula	$C_{17}H_{24}F_3NO_3S$
Formula weight	379.43 g/mol
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal size	0.138 x 0.180 x 0.226 mm
Crystal habit	clear colourless block
Crystal system	orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 5.3465(5) Å α = 90°
	b = 18.0649(19) Å β = 90°
	c = 37.732(4) Å γ = 90°
Volume	3644.3(6) $Å^3$
Z	8
Density (calculated)	1.383 g/cm^3
Absorption coefficient	1.996 mm^{-1}
F(000)	1600
Theta range for data collection	2.71 to 70.07°
Index ranges	-6<=h<=6, -21<=k<=21, -46<=l<=43
Reflections collected	74476
Independent reflections	6889 [R(int) = 0.0358]

Coverage of independent reflections	99.8%
Absorption correction	Multi-Scan
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	6889 / 0 / 467
Goodness-of-fit on F^2	1.056
Δ/σ_{max}	0.001
Final R indices	6826 data; $I>2\sigma(I)$ R1 = 0.0240, wR2 = 0.0620
	all data R1 = 0.0243, wR2 = 0.0621
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0328P)^2+0.9860P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.052(3)
Largest diff. peak and hole	0.295 and -0.236 eÅ^{-3}
R.M.S. deviation from mean	0.039 eÅ^{-3}



Thermal ellipsoid plot at 50% probability level. The N-H hydrogen atom was found in the residual density map and refined isotropically. The disordered CF_3 group was refined with a population of 0.54950 on the main domain using restraints (RIGU, SIMU, SAME).

Data collection and structure refinement

Identification code	v20102_1	
Chemical formula	$C_{16}H_{21}F_3N_2O_3S$	
Formula weight	378.41 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.030 x 0.120 x 0.230 mm	
Crystal habit	clear colourless plate	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 13.6461(5) Å	α = 90°
	b = 5.0549(2) Å	β = 112.0680(10)°
	c = 13.6638(5) Å	γ = 90°
Volume	873.47(6) $Å^3$	
Z	2	
Density (calculated)	1.439 g/cm^3	
Absorption coefficient	2.101 mm^{-1}	
F(000)	396	
Theta range for data collection	3.49 to 66.57°	
Index ranges	-16<=h<=16, -6<=k<=6, -16<=l<=16	
Reflections collected	22415	
Independent reflections	3054 [R(int) = 0.0373]	
Coverage of independent reflections	100.0%	
Absorption correction	Multi-Scan	

Max. and min. transmission	0.9400 and 0.6440	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3054 / 115 / 260	
Goodness-of-fit on F^2	1.048	
Δ/σ_{max}	0.001	
Final R indices	2976 data; $I>2\sigma(I)$	R1 = 0.0232, wR2 = 0.0593
	all data	R1 = 0.0241, wR2 = 0.0601
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0313P)^2+0.1918P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.057(7)	
Largest diff. peak and hole	0.176 and -0.201 eÅ^{-3}	
R.M.S. deviation from mean	0.032 eÅ^{-3}	

IX. DFT Calculations

All calculations were performed using ORCA 4.0.1.2 with the BP86 functional, the def2-TZVP basis set for all atoms, dispersion correction with Becke-Johnson damping (D3BJ), and the RIJCOSX approximation to speed up optimizations. Solvation (CPCM/SMD(THF)) was used for geometry optimization. In cases where the crystal structure was available, the experimental coordinates were used as the input. Calculation of the predicted redox potentials of the copper complexes was conducted through a theoretical redox reaction with ferrocene/ferrocenium (Fc^+/Fc). The predicted reduction potential of the photocatalyst **P**Cu^{I}(OPh) was first calculated to validate the relative accuracy of the computational method (experimental Cu^{II}/Cu^{I} potential: 0.0 V vs Fc^+/Fc; calculated: –0.1 V vs Fc^+/Fc; $\Delta E°_{Expt–Calc}$ = 0.1 V or 2.3 kcal/mol).

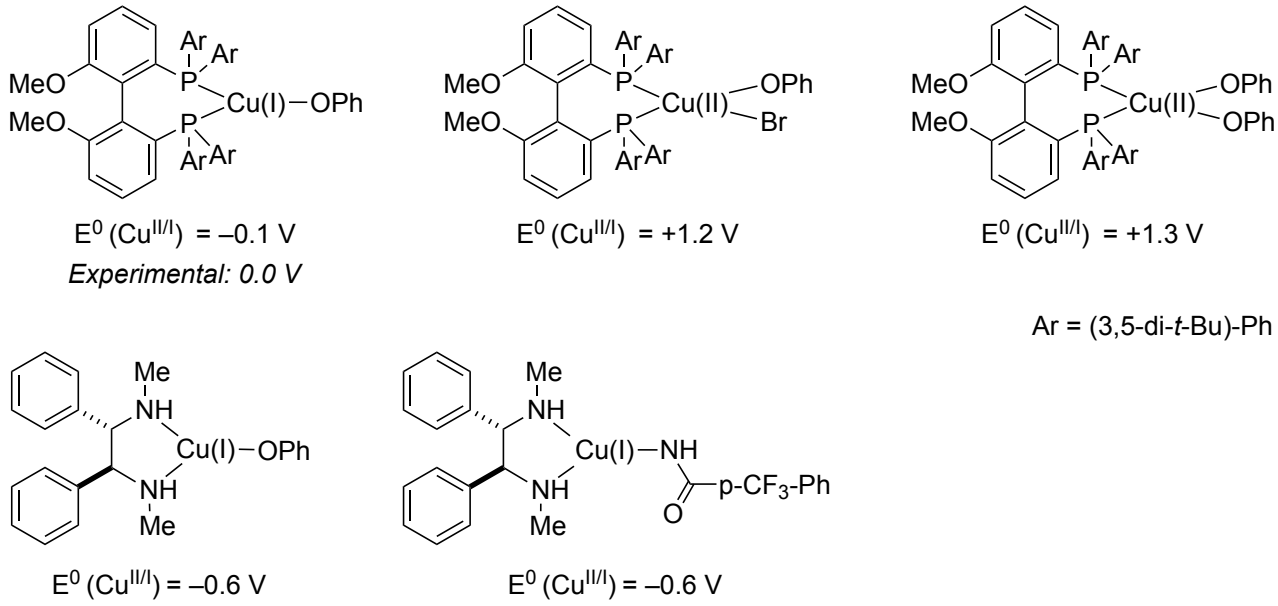


Figure S3. Calculated redox potentials of copper complexes (vs Fc^+/Fc).

Coordinates of the optimized geometries**.**

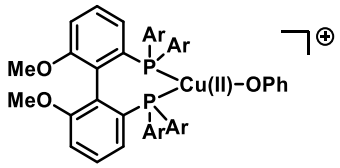
Ferrocene:

Fe	-1.75206296540367	-2.25720638957861	2.26115553705769
C	-2.51233773723522	-3.99537680099411	1.50383549407711
C	-0.35623472245267	-2.64564548316469	3.70132991977051
C	-1.48399447510705	-3.47896848148143	0.64581143981547
C	-3.54066951709310	-3.00001828129877	1.61214889829030
C	-1.62762834763110	-2.34981594774379	4.29799672363499
C	0.03651751527489	-1.51433021019807	2.91013870484520
C	-1.87649517892793	-2.16458753109719	0.22433085233373

C	-3.14787981304946	-1.86868039508537	0.82101127552900
C	-2.02010660556603	-1.03545222424721	3.87648862002775
C	-0.99184751279216	-0.51899018781870	3.01840298405258
H	-2.50259679356031	-4.96059537245075	2.00318813972205
H	0.19985773343380	-3.57329461170305	3.80960421705337
H	-0.55888256991057	-3.98457850537199	0.38130894247548
H	-4.44598768505324	-3.07950709265534	2.20814806940970
H	-2.20348724758781	-3.01455350790955	4.93690782672258
H	0.94184206002129	-1.43485127981454	2.31414430258721
H	-1.30066611620604	-1.49987184909892	-0.41464940634877
H	-3.70384326153520	-0.94095929084514	0.71284049387632
H	-2.94516300306265	-0.52977614486534	4.14111944951954
H	-1.00171530555576	0.44616373042255	2.51893753554820

Ferrocenium:

Fe	-1.75203230220716	-2.25724910219102	2.26120675834595
C	-2.51657516949779	-3.99402369384522	1.46401843631483
C	-0.33158029579435	-2.62382233693625	3.78206455188070
C	-1.51255408890143	-3.48898246034988	0.57303366650080
C	-3.54914963731798	-2.99773230671812	1.56818453570083
C	-1.58224593847042	-2.31704171659213	4.39164534470360
C	0.04502328545923	-1.51663643784433	2.95414183729940
C	-1.92183812147410	-2.19727845811302	0.13076793383130
C	-3.17244031107450	-1.89044507448159	0.74043479442749
C	-1.99160045541679	-1.02537324440122	3.94927642047811
C	-0.98762110011188	-0.52038984407802	3.05819664084164
H	-2.49296478034789	-4.95020725997261	1.97789828269246
H	0.20992295821771	-3.56041986013246	3.88077239691930
H	-0.57731787149595	-3.97959444083882	0.31895353881824
H	-4.44463007478724	-3.06352183047614	2.17885138257691
H	-2.16279970449681	-2.98687561170423	5.02020622137196
H	0.94050797718858	-1.45069193256373	2.34349839761126
H	-1.34094757500016	-1.52719961260276	-0.49721817934272
H	-3.71395257842150	-0.95385162127925	0.64165443557734
H	-2.92717352164179	-0.53510127403728	4.20277331181564
H	-1.01141224340781	0.43554226215807	2.54383931163495



Ar = 3,5-di-*t*-Bu-Ph

Cu	7.82094370729169	10.91652892954691	3.26439883527991
P	8.48354169670202	11.46620063695069	5.33620234984442
P	9.23284512584133	9.19251251438793	3.03568531049561
O	11.63170998056505	7.61437456371597	6.63139882036296
O	12.57125483822461	10.40620532453828	6.78897077737201
O	6.65862746904137	11.62745524596446	1.99344550602289
C	9.88681466880073	12.58370551977064	5.08288249577145
C	10.17129252485469	12.94844567856478	3.76152105214322
H	9.59944641558045	12.49850166565468	2.94909007536790
C	11.17386495077524	13.87396693594942	3.47004103969005
C	11.86441717971040	14.43849793270977	4.55186855461607
H	12.63241074326848	15.18510457233764	4.34297704457920
C	11.61351480061055	14.08493369137329	5.88810141219095
C	10.62649534228279	13.12507590530072	6.14303007767823
H	10.43025487610630	12.79464449261804	7.16089777109889
C	11.50327184408512	14.28356463415072	2.03096923303055
C	11.18442099580488	15.78269339863255	1.85617795791154
H	11.42654441795444	16.10635732955140	0.83250261013562
H	11.76240703885316	16.40450227581785	2.55384754800368
H	10.11542616528422	15.97560414804174	2.02910340868992
C	13.00179134004448	14.03954796495796	1.76538104497169
H	13.24934092295299	12.97585906021661	1.89023951330694
H	13.63799899814859	14.61845092220034	2.44908585932874
H	13.25966103577601	14.33352697946097	0.73682520257774
C	10.68534242924813	13.48699349290234	1.00286956105284
H	10.97660070836539	13.79368806465857	-0.01154703647384
H	9.60597012595962	13.67207282331995	1.10314775125067
H	10.86399816972530	12.40478580099152	1.08642939687186
C	12.36551502499573	14.79762749809843	7.01898701221348
C	12.11069424898272	14.14402392423081	8.38491841546991
H	11.05562223211956	14.21225050573119	8.68795175807259
H	12.70305736582679	14.65691371232630	9.15581200182446
H	12.39903976018775	13.08319017347573	8.39075983674195
C	11.87601733724215	16.26098428117375	7.07183479628189
H	12.07876449539516	16.79063604018464	6.12957895694496
H	12.38544222479817	16.80394050564592	7.88198213423921

H	10.79240172470605	16.30798613570315	7.25607600187774
C	13.88145958651845	14.78547870203079	6.74529695945973
H	14.26743673750657	13.75714059722745	6.68375042014578
H	14.41787076445053	15.29916411732384	7.55674237314150
H	14.13699682320887	15.29444322441532	5.80571399259915
C	7.15358161456386	12.36399695821620	6.17945472402232
C	5.84474204320166	12.13379250094788	5.73428400923224
H	5.68087265775017	11.44957187161960	4.90099591247507
C	4.76372831033295	12.79749132199413	6.32482688632660
C	5.04449070562263	13.69784289615063	7.36278506489582
H	4.21316882183468	14.23105619852223	7.82561095249827
C	6.34571168775707	13.95558736486285	7.82369947431132
C	7.40356296131037	13.27117297239894	7.21603219734612
H	8.42576932542905	13.44548186434027	7.54067382318087
C	6.57062523742779	14.96265990498943	8.95769672635235
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H	6.24139988084074	13.48706405059201	10.54594784661098
C	5.99248873264958	16.33232215976028	8.54224656349598
H	6.47510473593177	16.70302120128647	7.62591601111225
H	6.16230212772745	17.07091235409442	9.34014360513179
H	4.91002002854085	16.27947485660188	8.35937760297962
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H	8.62212637943599	15.51448088169475	8.41007121482515
H	8.52408974064796	14.20147722214760	9.61855266892865
H	8.18040468672318	15.87668716315696	10.08900601648163
C	3.32002316298292	12.59766132549244	5.85016274466724
C	3.21142060223514	11.51841697072554	4.76361852412719
C	2.44191544154698	12.18009730927407	7.04744714086405
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C	10.17148140544494	9.38773593262633	6.13092229506758
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C	13.08817174248731	10.45812731356562	3.14387669663964
H	13.84986661339137	10.71751278589822	2.40846929463958
C	11.85447578753191	9.97542889461327	2.72169295981038
H	11.64858558608950	9.86369726865811	1.65794616209869
C	10.87749225036633	9.61957088081025	3.67011923172326
C	12.24263719144931	6.80270022366343	7.64506238136996
H	11.62930101301328	5.92666750820726	7.90272740490225
H	12.43485426476181	7.39581819951432	8.55169845193389
H	13.19316559996519	6.46347713627085	7.22055656679993
C	13.89390017216603	10.68588037223785	7.26340317578958
H	14.60051141388582	9.90635087762024	6.93843388626110
H	13.82373288815655	10.68423539262655	8.35633795100652
H	14.25074216038221	11.66940385351044	6.92365509436234
C	8.55321833706847	7.80636612885387	3.97505126858560
C	9.30830353026906	6.66719662245324	4.29460197339061
H	10.36508795734563	6.63371138029685	4.03544546037816
C	8.70599591291514	5.59770861248754	4.95821834666650
C	7.34964001578942	5.71683971426477	5.32173498933362
H	6.88354531669006	4.89056536058312	5.85691502797549
C	6.58399604594791	6.85105117672443	5.03987868955402
C	7.21088922233010	7.89436797374686	4.34431302737713
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H	9.33970298720535	2.19511518366541	4.78836887686077
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C	5.12230427645637	7.00880963773638	5.47264131320046
C	4.56720040365215	5.73339693407198	6.12127552305970
C	5.03747335411103	8.16259953617710	6.49355194829635

C	4.25774274092533	7.35392176384324	4.24320493659278
C	9.47697655016631	8.66332975487309	1.31919917232961
C	9.02263841206171	9.50507289684768	0.30448533298183
H	8.49235528998383	10.41981195299863	0.57510830433963
C	9.23603158428297	9.17647668201182	-1.04541682261829
C	9.90686501887955	7.98301518615810	-1.32498853627799
H	10.08391494891555	7.71058099493698	-2.36462089941579
C	10.36121685661700	7.10714616364238	-0.31767781836296
C	10.14085934450127	7.46436158972971	1.01207975116785
H	10.48862600159687	6.82126750745913	1.81696926708707
C	8.69964818609634	10.10902311963025	-2.13678062440411
C	7.15777348735682	10.08184546975825	-2.07388033469394
H	6.72961575809931	10.77457969383859	-2.81363368014691
H	6.78553789635249	10.36810771965172	-1.08093091296948
H	6.77710296176205	9.07258108038168	-2.29136143116474
C	9.20404287022172	11.54413760268758	-1.88276152424965
H	10.30266368291383	11.58738424787473	-1.91900301821032
H	8.88321256986766	11.93076862611750	-0.90659434788833
H	8.80802517140139	12.22721470444127	-2.64922112196813
C	9.14354752953781	9.67797502393213	-3.54170152450145
H	8.75155851444542	10.38816399346912	-4.28394674067509
H	8.76265360933198	8.68141770417466	-3.80785534824105
H	10.23978366009744	9.66640442667800	-3.63735273127584
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H	13.04299961829627	6.79217354892500	-0.85672580025272
C	10.16674309587277	4.96382928350332	-1.60428853266586
H	9.88423643501504	5.49935744339992	-2.52162213556982
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H	12.15486071676621	5.52281888468040	1.19619680465692
H	11.98046623227780	4.06086689640402	0.20811976042505
C	6.81866328799200	12.90319044694532	1.64755848639562
C	7.14512723506945	13.90127876196242	2.60351238959599
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C	6.64600054834430	13.29506551961086	0.29603968506217
H	6.37455764248706	12.53669252793327	-0.43822200259706
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H	4.31073462367007	6.55815215065928	3.48505061076801
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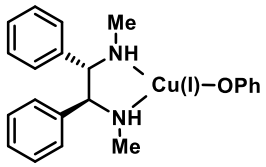

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C	-1.27135178456849	0.25379838671477	-1.50969725960334
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C	-6.27913697449703	1.28777836615425	-2.35671937649341
C	-4.68398927026528	-0.42339025215705	-2.97750167155528
C	-4.13371909940551	1.15105222095863	-1.23667574749275
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H	-5.64042584503055	2.62540613383884	-0.78246380572758
H	-6.62245101450231	-0.19090669132869	-3.89816867931308
H	-7.24771937342100	1.77226814254238	-2.48808636894838
C	-1.16218547080344	1.47506362676966	-2.39750832647438
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H	-0.17448759045436	4.74173209504473	-2.17605515068581
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H	-1.39515453684662	0.60124618284938	-0.47403756915304
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H	0.70584544402268	-0.03733255087185	-3.44622626780494
H	-0.12900062680187	-1.61440283200197	-3.31144266463926
C	-3.16787450069649	-1.47152108915788	0.43055301267577
H	-2.63897162059212	-0.66305227440203	0.95447568222220
H	-3.10928197660128	-2.36942165998586	1.05956169989573
H	-4.22706399474445	-1.18177266399831	0.32359183412329
H	-2.94352893547296	-2.59022010311106	-1.26586690283348
H	0.70598255274994	0.04355994720651	-1.01389709769707
C	-3.07788717403414	-6.54705773020700	0.67341704746694
C	-2.58946850808082	-5.95005680783740	-0.49637204321426
C	-1.63037317296547	-4.93903768974690	-0.43700998476560
C	-1.12064431906642	-4.47271791595460	0.80712965904601
C	-1.62163190741602	-5.09905542260495	1.98074813702749
C	-2.57856261696456	-6.11090033225801	1.90902776923435
H	-3.82879979834362	-7.33716706982511	0.62339282402009
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H	-1.24745754479671	-4.47964763508283	-1.35317334885479
H	-1.24296234189207	-4.75886430911101	2.94720120912922
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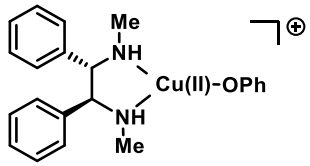

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C	-1.97507093235485	0.14623685384924	-1.12871385437912
H	-3.38200013097102	-1.08908883259194	-2.19918213346753
C	-4.32532290850878	0.79710994193952	-1.91754019514555
C	-6.08607457161847	2.77923619822173	-2.84695147577037
C	-5.31704007308788	0.48523615026587	-2.85770610581890
C	-4.22560634720395	2.11408036061388	-1.44548157964122
C	-5.10092895261268	3.09882168336147	-1.90750953627262
C	-6.19352660795269	1.46867506652855	-3.32146925251901
H	-5.39351280215766	-0.53577070806813	-3.23842196266875
H	-3.45815529315514	2.38520344495532	-0.71958688878474
H	-5.00953167132111	4.12005362204118	-1.53546578644582
H	-6.95518192400650	1.21302151809378	-4.05977125481177
H	-6.76475667593922	3.55124510049937	-3.21200772818425
C	-1.30396156836491	0.91240585253190	-2.24557411542961
C	0.04464808148867	2.33516394954095	-4.25713513869768
C	-0.37978311906066	1.91265602638667	-1.91342932471629
C	-1.54699234847149	0.63283723720086	-3.59752565341805
C	-0.87748362571839	1.34049940144598	-4.59715256341059
C	0.29283003227588	2.62052245366033	-2.91131888045391
H	-0.19282379990301	2.14396529511492	-0.86206187146959
H	-2.26758542565407	-0.13480428888344	-3.88276912974190
H	-1.07990446708443	1.11684011529930	-5.64555537328096
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H	0.56415934543763	2.88998812249556	-5.03926406063055
H	-1.98924865382558	0.79412282396915	-0.24053663538662
O	-1.68398857971789	-3.57796341742058	1.30194992629142
C	-0.62417891798056	-1.90240716280325	-1.77464492285709
H	-0.14535165351536	-2.77755492100360	-1.31869955108635
H	0.12588676232243	-1.35270385883901	-2.36020739426503
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C	-4.39770808445635	-0.13855780276445	0.90656607882787
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H	-4.77520487804485	-0.78027806498100	1.71115999498295

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H	-4.73915338985951	-1.58233039983449	-0.50133071042307
H	-0.42887042883448	-0.75396673854934	-0.08925389954984
C	-0.14604026500955	-6.94824224322553	-0.55078725368932
C	-1.23309757307944	-6.27473303643166	-1.12963208271501
C	-1.76770679938036	-5.15017732956671	-0.51343957280162
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C	0.40236414330088	-6.48196077839392	0.65366377139475
H	0.26657366916146	-7.83474756614681	-1.03252047447050
H	-1.66742040519215	-6.63923346646924	-2.06117173585026
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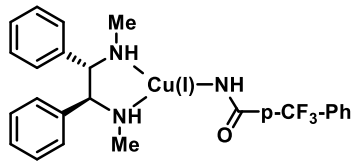

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C	-1.70795426285397	0.63298757989018	-1.34547062459639
H	-3.17748367850924	-0.88628067721233	-1.77574669643932
C	-4.16800050137031	0.97633448540234	-2.00937213035874
C	-6.13706221759855	2.53497707125008	-3.28648115701285
C	-5.21915465256705	0.37032276775639	-2.71177913187642
C	-4.11840524151045	2.37711247549840	-1.95426516270221
C	-5.09487073762589	3.15058114774542	-2.58642017711718
C	-6.19690530345942	1.13878904799768	-3.34703528280033
H	-5.26487523807307	-0.72074790647180	-2.76590988019187
H	-3.30835347356450	2.87619287627607	-1.42068114981799
H	-5.03975921959533	4.23975026665815	-2.53390607332774
H	-7.00336482414643	0.64747539461952	-3.89440884710978
H	-6.89734930351351	3.13947115830292	-3.78369260069634
C	-1.24871028007835	1.10322351538513	-2.70751554372534
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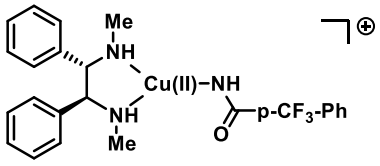

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H	-3.44986895253360	-1.04024190186400	-1.98556222269702
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C	-3.66089683038442	2.24784708270336	-1.18172698931700
C	-4.49845872198976	3.33431314142922	-1.44114361062502
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H	-7.08338399148989	1.68776569714413	-2.93460618791712
H	-6.38333429745864	3.98842934564285	-2.27407469312968
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C	-0.17319044796075	1.79123962509043	-4.95588522550736
C	-0.07557656142191	1.47406742865663	-2.56011595200326
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H	1.30597176741983	2.70562660555785	-3.66913090389673
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H	-1.39206257354465	0.65322240157303	-0.49623632116046
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C	0.29485804483082	-5.51008302983213	2.93654612460203
C	-2.00208579995918	-5.70879417022297	3.69088534579373
C	-1.63181402746783	-6.73510857806682	4.55619159002218
C	0.67094092546184	-6.53200532966235	3.80230419062038
H	1.03467670947697	-5.02749970645139	2.29922416927328
H	-3.04871650779077	-5.40643271142372	3.64559167606461
H	-2.38155341021489	-7.21852164117585	5.18082090660407

H	1.71035400296472	-6.85626927089496	3.84603251004381
C	0.13060544658315	-8.22383032109414	5.56899616308350
F	0.70024968605100	-7.69517929196187	6.69768537561966
F	-0.90560987750031	-8.99883143417198	5.98340958061566
F	1.06047375718778	-9.05942477405281	5.02702844166380
C	-0.86294662657714	-2.26552468710133	-2.15156531621637
H	-0.36967293685427	-3.16943005939863	-1.77746453458079
H	-0.26751236520755	-1.84238604842596	-2.97192476439899
H	-1.85499089067897	-2.53751290532546	-2.52990341167296
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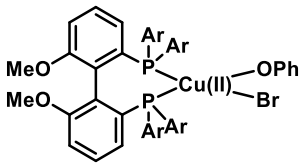

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O	11.34551837757486	7.68458522826993	6.61334014479140
O	12.58364664725526	10.52352612810739	6.75699874151695
Br	7.82623268303334	12.94136541170938	1.75142599060135
C	10.19844154197163	12.87539843950677	5.20336255023146
C	10.74384392239273	13.27351803283878	3.97878433091259
H	10.25878878869178	12.94428952645400	3.06185100572118
C	11.87351075657330	14.09582535538647	3.94526261251146
C	12.40183635607223	14.53598525901922	5.16868587172950
H	13.25284514500234	15.21864719589575	5.15201117273862
C	11.87842807737846	14.14746034788781	6.41194919573864
C	10.77795357052226	13.28012136253549	6.41400318911131
H	10.36443946861849	12.91354372752307	7.35156575356219
C	12.50780444106871	14.54262838465314	2.62306708069297
C	12.30272557774927	16.06326874048883	2.46242224912287
H	12.75525496887756	16.41556120818042	1.52239485990961
H	12.76686877425720	16.62100204476924	3.28902217163723
H	11.23203374315955	16.31570775460855	2.44171786402960

C	14.01736373698886	14.22978628890069	2.63827130998313
H	14.18946683456172	13.15139784652187	2.76600948099625
H	14.54141248076653	14.75583139257410	3.44778186692389
H	14.47816437975589	14.54011513355064	1.68804919594299
C	11.87850256323947	13.82074475439899	1.42133348227130
H	12.36543738169496	14.15369404704579	0.49305624529508
H	10.80140056121486	14.02237041496008	1.32797265601214
H	12.00936252853176	12.73148019288814	1.50275963082361
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C	11.99068358999533	13.94944436744520	8.94712700089852
H	10.90198562547496	13.99361269240947	9.09186725448982
H	12.45744719696883	14.37091799797257	9.84921283161315
H	12.28072105520753	12.89132753467602	8.87952979132632
C	11.93204454670293	16.19188785668940	7.82913102006471
H	12.24708164573628	16.79737458087532	6.96616991087964
H	12.32761927363490	16.66635690842744	8.74073486381383
H	10.83359087419370	16.22025139061606	7.87747949506232
C	13.98522171750563	14.76566687905705	7.69246138717427
H	14.40344391054811	13.75582508413217	7.57912352557218
H	14.36282309023469	15.18059032970722	8.63901766115419
H	14.38463101007043	15.39023650545671	6.88234817387429
C	7.32859178931363	12.79556722755745	5.87056577614420
C	6.05330742428045	12.30349455495176	5.57808305671108
H	5.95547596241800	11.38146362790095	5.00063056651303
C	4.90289578047099	12.99560976054847	5.97855699232961
C	5.07512700581780	14.19395693441085	6.68000113454862
H	4.19389246434410	14.75706903499338	6.98525461176417
C	6.34751182161440	14.71574650778181	6.98575849401320
C	7.47546661117271	14.00108435067279	6.57008745215083
H	8.47517842436305	14.38262228360424	6.76731149081624
C	6.45552839029820	16.05734774352132	7.72152832880879
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H	4.61498996919193	15.76664265300697	8.89724067756037
H	5.75006549529191	16.94890105173475	9.58206908839288
H	6.09530835540615	15.20498579495673	9.70890875741065
C	5.84617231759333	17.16132814642800	6.83123835261925
H	6.38523308966290	17.23378962124623	5.87544051081712
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H	4.78779386063787	16.96506344629408	6.60900485697952
C	7.91275318794729	16.43009930543142	8.02876994640670
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C	9.02409685529300	10.47228838417755	6.33210236495422
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C	8.28187336878140	9.05027525990556	8.14203519698716
H	7.57298060355742	8.83026826678621	8.94175207200419
C	9.35572430187451	8.18659820112586	7.92130361651460
H	9.47106315302118	7.29928382438238	8.53907431317425
C	10.27374169861293	8.47010880194010	6.90011112142186
C	10.11686382612218	9.61506742306718	6.08600594762260
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H	13.91440110265641	10.59065696059131	2.37637902011246
C	11.89098878627296	9.93195892117742	2.69984852819380
H	11.69875319677028	9.75125471244582	1.64322657291467
C	10.88867116236822	9.68088308172722	3.65036686222224
C	11.53787919518815	6.51949818617814	7.41774904992859
H	10.67207458300637	5.84381996522797	7.35100882292692
H	11.71492272188372	6.78757290076499	8.47161566749783
H	12.42926959292330	6.02295345670154	7.01995420338838
C	13.88903196648108	10.89658844615772	7.20609485656551
H	14.63297460854920	10.12837681623678	6.94038997049536
H	13.82095399133766	10.97462724490680	8.29647518832000
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C	8.77047940966832	7.72601424037525	4.03491307917930
C	9.63494256791808	6.62343680675251	3.99951824306540
H	10.58472021610995	6.70881143151218	3.47395556842058
C	9.26698803052359	5.41984167468904	4.61257640712945
C	8.04901658548339	5.38994714180559	5.30950159155981
H	7.75054748754994	4.46227137802357	5.79821346964404
C	7.18270391769781	6.49140574103896	5.38142380670721
C	7.54590149550939	7.66094810097516	4.70649351688980
H	6.88918589842563	8.52853648530611	4.67591981615426

C	10.09654596181633	4.14000191842118	4.42911366351505
C	11.54038294950157	4.44706010748976	4.00000983961902
H	11.58223565070190	4.93758612038078	3.01700880589572
H	12.11125489077656	3.51078682375826	3.92088786317633
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C	9.42107510332108	3.30569720179988	3.31798516649784
H	9.40484093994712	3.85728192526811	2.36672297801011
H	8.38328638817938	3.05853642172410	3.58299212243761
H	9.96796431369360	2.36435081534852	3.15423497790077
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H	10.76125775015392	2.40665813797087	5.56189131184679
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C	4.94894487390352	5.36988553335833	5.42377417681019
C	9.23137073076866	8.79049719735772	1.37104136569129
C	9.50679174099865	9.80395602365752	0.43452660671685
H	9.74091910028064	10.80565757184709	0.78982048237667
C	9.40469258466196	9.54987318680773	-0.93255717139681
C	8.99142201180848	8.26724253454103	-1.33759894802916
H	8.88415499359875	8.06964777259949	-2.40355031987297
C	8.68809268376212	7.24801104136046	-0.42799102452708
C	8.81503008942545	7.52860058536773	0.93905419843073
H	8.57059114800413	6.77096555692165	1.67935224328253
C	9.67152604700570	10.63544688956533	-1.98345044423624
C	8.34187419840868	10.98293000005802	-2.68536863042323
H	8.51407566644495	11.72223718345971	-3.48287512976997
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H	7.88042108504020	10.09529619835670	-3.14154379437474
C	10.24413491577649	11.91622750562716	-1.35589140163829
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C	10.67804818934056	10.11058550553408	-3.02762908777637
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H	11.63131483939232	9.83311850981848	-2.55328232639919
C	8.28046727739143	5.84212971588287	-0.88536504279725
C	9.55525164642246	4.97272588610430	-0.94462903753028

H	10.27603180837405	5.37431528752096	-1.67281207866902
H	9.30654638503401	3.94122292466537	-1.23916470635090
H	10.05092895127415	4.93803313784966	0.03678518394816
C	7.62370619782091	5.86365045782928	-2.27582877316524
H	8.32061449855700	6.19049366329403	-3.06014623359918
H	6.74748993310915	6.52827753862923	-2.29312471584297
H	7.28914043377199	4.85052976075272	-2.54217662780043
C	7.28939620744542	5.20798399249248	0.10863498469598
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H	3.47687411987766	10.98518339713192	7.23659551244287
O	6.19142241172181	10.02614094338721	3.01788222628842
C	4.75128397454019	8.00031275706445	-0.31275652899341
C	5.61913970949304	9.09019378863383	-0.47249966371281
C	6.10110317854720	9.78743001454562	0.62938329435629
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C	4.88669293155366	8.27562607930610	2.09518319778438
C	4.38842425481538	7.60434218116052	0.98204422230844
H	4.37511180244069	7.45918818738307	-1.18192571776288
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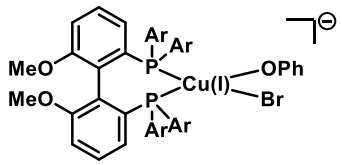

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P	9.08064957301254	9.33788744547748	2.86119999651323
O	11.24276039995074	7.80844505850561	6.56358809696819
O	12.37734807615491	10.46903921191481	6.69620284101746
Br	7.70179366488028	12.77615961882171	1.25434057163440
C	9.99846843106488	12.82387073097917	4.98978190674084
C	10.49101389132163	13.19950184326161	3.73469538862263
H	9.93112879656394	12.89024168351767	2.85108896520901
C	11.66626407237334	13.95147520862834	3.62764445426322
C	12.30383772209944	14.34409312253571	4.81331907641213
H	13.20253366485850	14.95840663026434	4.74259664661174
C	11.83725941478309	13.97899045842469	6.08575024499113
C	10.68427627311930	13.18738304144155	6.15684114320029
H	10.32269646952083	12.82724312466537	7.11754517703766
C	12.22742301151599	14.38152105242841	2.26611877181999
C	11.91757263410275	15.88051996896125	2.06553634996505
H	12.31896087954635	16.23476969785580	1.10269424284045
H	12.36397513399741	16.49131859879037	2.86444543688580
H	10.83161616712038	16.05818664036239	2.06893152046780
C	13.75223169724207	14.16714354136070	2.22339335794260
H	14.00138999700893	13.11362752534609	2.41637932240527
H	14.28356671374214	14.78406117697193	2.96124374974990
H	14.14291969160531	14.43415172188433	1.22935727533298
C	11.59639447994878	13.58421719677438	1.11397836924020
H	12.03056442129430	13.91360074800488	0.15781375260659
H	10.50645440495004	13.71982217402477	1.05606513635935
H	11.78483634401087	12.50665781482272	1.22275143203459
C	12.53969288520686	14.50857134420616	7.34454266833399
C	12.09246211331478	13.75530723205676	8.60637886835369
H	11.02587817388874	13.91184994555781	8.82315458805850
H	12.65964897843119	14.11658956968735	9.47688970122406
H	12.26411159357452	12.67338709893614	8.51019005516491
C	12.17865127607296	16.00163993248763	7.49976212110133
H	12.50090688700969	16.58253799020592	6.62292434583078

H	12.66509373610784	16.42946676182583	8.39054802337938
H	11.09185615526717	16.13198050172567	7.60691923660732
C	14.06969757400876	14.38481462184255	7.22286882371095
H	14.37571669481268	13.33852285606308	7.08250257024529
H	14.55193261847348	14.75813327695094	8.13893892114595
H	14.47063831901224	14.96925157065476	6.38343521729335
C	7.22479812406935	12.88625133459220	5.92066746755486
C	5.88848824584652	12.56430761340615	5.66322211020304
H	5.66613592599473	11.78446264973043	4.92832641131375
C	4.84552533673813	13.24444435258068	6.31226947542844
C	5.17966431427926	14.26818987681773	7.20415602517010
H	4.38262019590731	14.81456822932576	7.70889505347865
C	6.51644157981789	14.63262696466428	7.46132893205456
C	7.53368561078245	13.92826634790971	6.80958649767540
H	8.57517944644048	14.19074407246018	6.98009849162338
C	6.80990635181987	15.77714198034526	8.44101879028076
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H	5.16297897642650	15.25337842738595	9.80084571198562
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H	6.75997878438575	9.49277835772388	1.05810198623346
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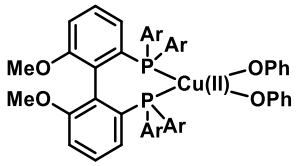

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P	9.35153046781556	9.19709869343482	3.12653768216614
O	11.54791960187790	7.62103134105728	6.77348123340103
O	12.55613774834561	10.34842365501510	6.98976626681068
O	8.11808908276764	12.31450208983773	1.93296304183613
C	10.05316894877258	12.60568558038823	5.23910041676145
C	10.50859104659869	13.00488414395755	3.97974616668009
H	9.96608036782812	12.66821313970356	3.09727307596786

C	11.63462934747679	13.82656927453431	3.86609173783036
C	12.25009988880749	14.26122604190168	5.04755999482522
H	13.11057098122288	14.92652808470854	4.97111181951272
C	11.80921807483065	13.87990676914680	6.32476199941068
C	10.70678958467620	13.02276441227179	6.40756082674130
H	10.34899223309166	12.67129130675697	7.37333456335418
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H	12.05445368140560	16.10470515023421	1.29171567789492
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C	13.69475868309455	14.22309440385664	2.46377921969446
H	14.05135154258437	13.21028857166383	2.70241235508618
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H	9.11015483489094	4.67142501749584	0.92226625981019
H	10.87990668186602	4.84339581042627	0.78591968282790
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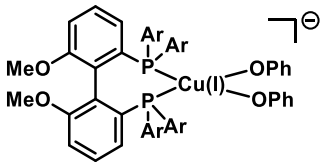

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H	10.34754234563115	12.89192836489194	7.42456953762431
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H	12.00964759480758	16.56833202232298	3.01354613294862
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C	5.06141793780118	13.98438609353726	6.79191823779254
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C	6.32219295011821	14.56657353140386	6.98214851118477
C	7.45525774142311	13.81887035104955	6.63334757439433
H	8.44738197778846	14.25488000859202	6.72623334776915
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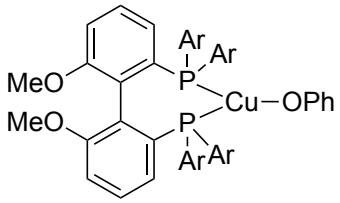
X. Mechanism Studies



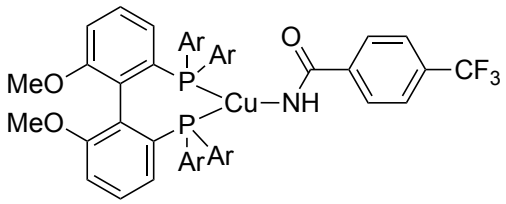
Ar = (3,5-di-*t*-butyl)phenyl

Preparation of PCu^{I}(OPh). In a nitrogen-filled glovebox, a suspension of CuCl (19.8 mg, 0.20 mmol) and *rac*-**P** (206 mg, 0.20 mmol) in THF (5.0 mL) was stirred at room temperature for 30 min, followed by the dropwise addition of a solution of NaOPh (23.2 mg, 0.20 mmol) in THF (5.0 mL). The resulting mixture was stirred at room temperature for an additional 30 min. The suspension was then filtered, and the filtrate was concentrated. To the residue was added pentane (8.0 mL), and the suspension was filtered again. The filtrate was concentrated to give the desired product as a light-yellow solid. 220 mg, 93% yield. Crystals suitable for x-ray analysis were collected from a saturated pentane solution at –20 °C.

^{1}H NMR (500 MHz, C_6D_6) δ 8.50 (s, 4H), 7.78 (t, *J* = 6.5 Hz, 4H), 7.62 (s, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.34 (s, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 6.92 (dd, *J* = 8.1, 4.3 Hz, 2H), 6.73 (t, *J* = 7.1 Hz, 1H), 6.60 (t, *J* = 8.0 Hz, 2H), 5.91 (d, *J* = 8.2 Hz, 2H), 3.16 (s, 6H), 1.35 (s, 36H), 1.21 (s, 36H).

^{13}C NMR (126 MHz, C_6D_6) δ 169.8 (d, *J* = 4.9 Hz), 158.1 (t, *J* = 5.0 Hz), 151.5, 149.6, 136.4, 132.4 (t, *J* = 15.0 Hz), 129.2, 128.8 (t, *J* = 9.2 Hz), 125.0, 124.6, 123.7, 119.8, 112.9, 111.5, 55.9, 34.7 (d, *J* = 62.2 Hz), 31.2 (d, *J* = 15.4 Hz).

^{31}P NMR (121 MHz, C_6D_6) δ –0.4.



Ar = (3,5-di-*t*-butyl)phenyl

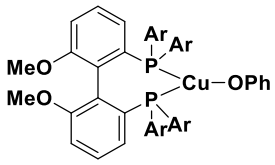
Preparation of PCu^{I}(amidate). In a nitrogen-filled glovebox, a suspension of CuCl (9.9 mg, 0.10 mmol) and *rac*-**P** (103 mg, 0.10 mmol) in THF (5.0 mL) was stirred at room temperature for 30 min, followed by the addition of potassium (4-(trifluoromethyl)benzoyl)-amide (22.7 mg, 0.10 mmol). The resulting suspension was stirred at room temperature for 30 min. The suspension was then filtered, and the filtrate was concentrated. To the residue was added pentane (8.0 mL), and the suspension was filtered again. The filtrate was concentrated to give the desired product as a white solid. 120 mg, 94% yield. Crystals suitable for x-ray analysis were collected from a saturated pentane solution.

^{1}H NMR (400 MHz, C_6D_6) δ 8.25 (t, *J* = 5.9 Hz, 4H), 8.01 (d, *J* = 8.0 Hz, 2H), 7.80 – 7.66 (m, 4H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 1.9 Hz, 2H), 6.96 (t, *J* = 1.3 Hz, 2H), 6.69 (dt, *J* = 8.7, 4.7 Hz, 2H), 6.37 (t, *J* = 8.0 Hz, 2H), 6.14 (s, 1H), 5.72 (d, *J* = 8.5 Hz, 2H), 2.98 (s, 6H), 1.12 (s, 36H), 1.08 (s, 36H).

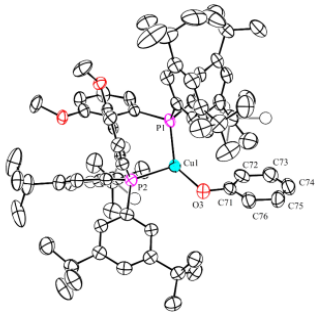
^{13}C NMR (101 MHz, C_6D_6) δ 171.0, 158.1 (t, *J* = 4.9 Hz), 151.1 (t, *J* = 5.5 Hz), 149.5 (t, *J* = 5.4 Hz), 143.8, 136.6 (t, *J* = 11.8 Hz), 132.6 (d, *J* = 6.3 Hz), 132.4, 132.2 (d, *J* = 2.6 Hz), 130.6, 128.9 (t, *J* = 9.1 Hz), 128.5 (t, *J* = 3.8 Hz), 124.7, 124.4 (q, *J* = 3.8 Hz), 124.0, 123.8 (t, *J* = 4.1 Hz), 111.4, 55.9, 34.9, 34.6, 31.3, 31.3, 22.4, 13.9.

^{31}P NMR (162 MHz, C_6D_6) δ –0.6.

^{19}F NMR (282 MHz, C_6D_6) δ –61.9.



Ar = (3,5-di-*t*-butyl)-Ph



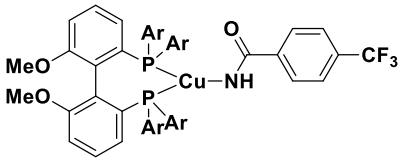
CCDC 2055329

Thermal ellipsoid plot at 50% probability level. The asymmetric unit contains one molecule of the copper complex and 2.5 molecules of hexane. Hydrogen atoms, solvent molecules, and minor domains of disordered fragments are not shown for clarity. Two disordered *tert*-butyl groups of the complex molecule were refined with a population of 0.71437 on the main domains. One disordered *tert*-butyl group was refined using restraints (SIMU). Two disordered hexane molecules were refined with populations of 0.62359 and 0.26359 on the main domains, respectively. The hexane molecules were refined using restraints (SIMU; DELU, SADI, SAME).

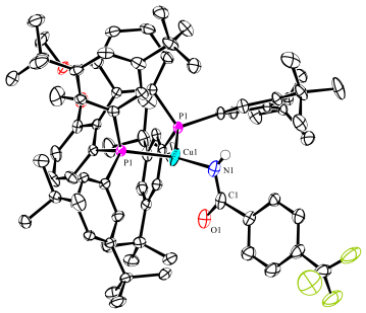
Data collection and structure refinement

Identification code	v19498	
Chemical formula	$C_{88.50}H_{131}CuO_3P_2$	
Formula weight	1368.41 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.143 x 0.167 x 0.353 mm	
Crystal habit	colorless blade	
Crystal system	monoclinic	
Space group	*P* 1 2_1/n 1	
Unit cell dimensions	a = 14.9725(7) Å	α = 90°
	b = 32.9930(15) Å	β = 112.268(3)°
	c = 18.2882(9) Å	γ = 90°
Volume	8360.4(7) $Å^3$	
Z	4	
Density (calculated)	1.087 g/cm^3	
Absorption coefficient	1.061 mm^{-1}	
F(000)	2980	
Theta range for data collection	2.93 to 67.03°	
Index ranges	-17<=h<=17, -39<=k<=35, -21<=l<=21	

Reflections collected	167471
Independent reflections	14461 [R(int) = 0.0802]
Coverage of independent reflections	96.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8630 and 0.7060
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	14461 / 384 / 1062
Goodness-of-fit on F^2	1.054
Δ/σmax	0.001
Final R indices	11008 data; I>2σ(I) R1 = 0.0723, wR2 = 0.1752
	all data
Weighting scheme	w=1/[σ2(Fo2)+(0.0718P)2+18.0601P]
where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.642 and -0.579 eÅ^{-3}



Ar = (3,5-di-*t*-butyl)-Ph



CCDC 2055330

Thermal ellipsoid plot at 50% probability level. The asymmetric unit contains half a molecule of the copper complex. Selected hydrogen atoms, solvent molecules, and minor domains of disordered fragments are not shown for clarity. Two disordered *tert*-butyl groups of the complex molecule were refined with populations of 0.90621 and 0.71171 on the main domains, respectively. The disordered amide fragment was refined with equal population on both domains. One disordered *tert*-butyl group and the disordered trifluoromethyl group were refined using constraints (EADP). The N-H hydrogen atom was refined isotropically on a calculated position by using a riding model.

Data collection and structure refinement

Identification code	V20061_1	
Chemical formula	$C_{39}H_{50.50}Cu_{0.50}F_{1.50}N_{0.50}O_{1.50}P$	
Formula weight	641.54 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.082 x 0.087 x 0.158 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 21.0986(17) Å	α = 90°
	b = 18.8131(14) Å	β = 114.530(3)°
	c = 20.3206(18) Å	γ = 90°
Volume	7337.9(10) $Å^3$	
Z	8	
Density (calculated)	1.161 g/cm^3	
Absorption coefficient	0.394 mm^{-1}	
F(000)	2744	
Theta range for data collection	2.12 to 30.55°	
Index ranges	-30<=h<=30, -26<=k<=26, -29<=l<=29	

Reflections collected	193361	
Independent reflections	11205 [R(int) = 0.0608]	
Coverage of independent reflections	99.7%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9680 and 0.9400	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	11205 / 0 / 507	
Goodness-of-fit on F^2	1.056	
Δ/σ_{max}	0.001	
Final R indices	9768 data; I>2σ(I)	R1 = 0.0426, wR2 = 0.1015
	all data	R1 = 0.0499, wR2 = 0.1052
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0400P)^2+9.0343P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.498 and -1.317 eÅ^{-3}	
R.M.S. deviation from mean	0.053 eÅ^{-3}	

Excited-state lifetime measurement of PCu^{I}(OPh) and PCu^{I}(amidate). A Q-switched Nd:YAG laser (SpectraPhysics Quanta-Ray PRO-Series; 355 nm) was used as the source of the excitation pulse in the Beckman Institute Laser Resource Center (BILRC; California Institute of Technology). Transmitted light from the sample was detected with a photomultiplier tube (Hamamatsu R928). All instruments and electronics in these systems were controlled by software written in LabVIEW (National Instruments).

After exciting the sample of **P**Cu^{I}(OPh) (0.38 mM solution in 2-Me-THF) at 355 nm, the intensity of the emission at 495 nm was measured. The excited-state lifetime of **P**Cu^{I}(OPh) complex was determined to be 4.6 μs.

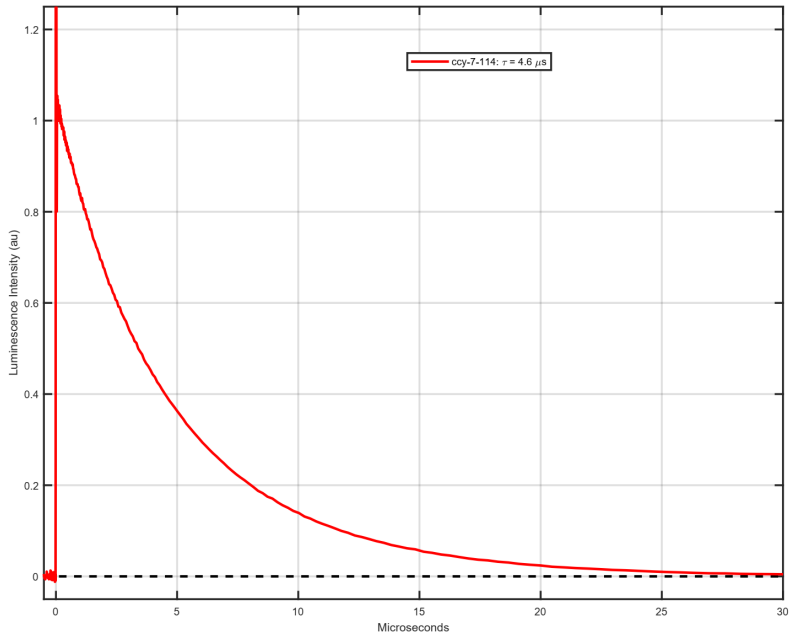


Figure S4. Plot of time-resolved luminescence decay of **P**Cu^{I}(OPh).

After exciting the sample of **P**Cu^{I}(amidate) complex (0.38 mM solution in 2-Me-THF) at 355 nm, the intensity of the emission at 500 nm was measured. The excited-state lifetime of **P**Cu^{I}(amidate) complex was determined to be 2.4 μs.

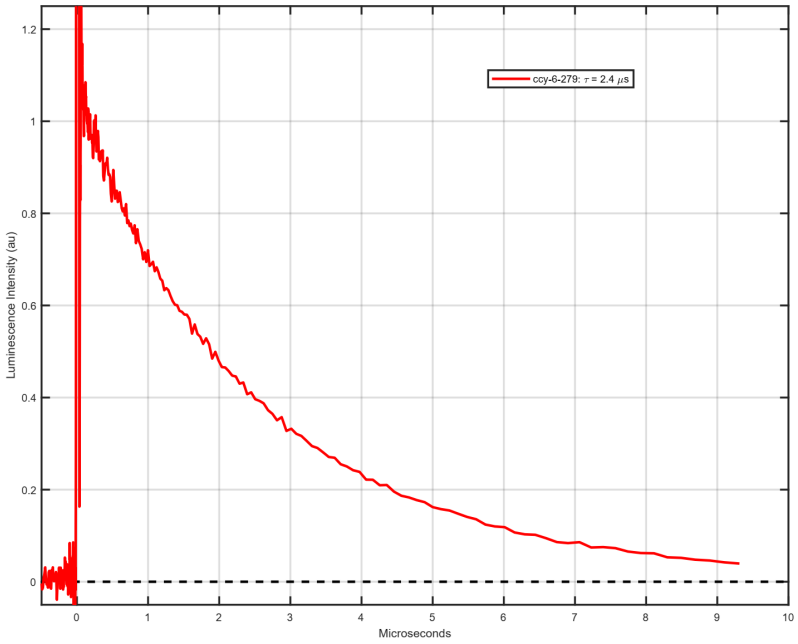


Figure S5. Plot of time-resolved luminescence decay of **P**Cu^{I}(amidate).

Stern-Volmer luminescence quenching of PCu^{I}(OPh) and PCu^{I}(amidate) complexes in the presence of a γ-bromoamide. Solutions of **P**Cu^{I}(OPh) (0.83 mM, 3.0 mg) or **P**Cu^{I}(amidate) (0.83 mM, 3.3 mg) with various amounts of 4-bromo-1-(indolin-1-yl)hexan-1-one (0.50 – 40.0 mM) in 2-Me-THF (3.0 mL) were prepared in 4 mL cuvettes in a glovebox. The emission spectra of the samples were then measured by steady-state fluorescence spectroscopy with irradiation at 350 nm for **P**Cu^{I}(OPh) and 400 nm for **P**Cu^{I}(amidate).

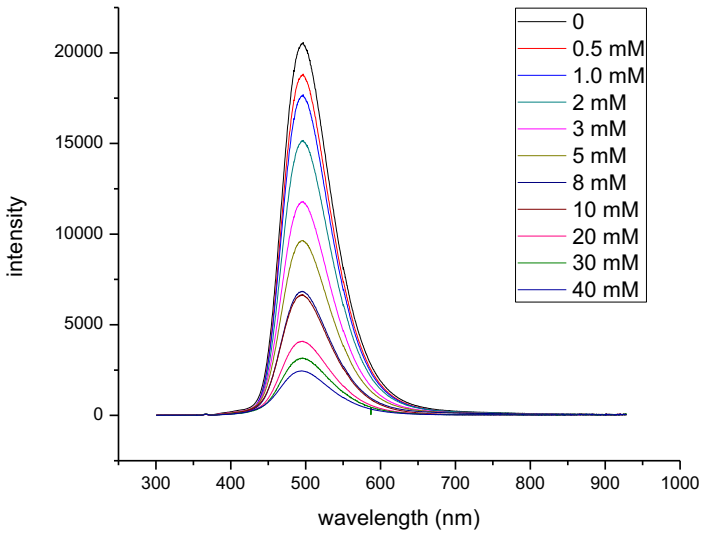


Figure S6. Emission spectra of **P**Cu^{I}(OPh) upon irradiation at 350 nm in the presence of varying amounts of 4-bromo-1-(indolin-1-yl)hexan-1-one.

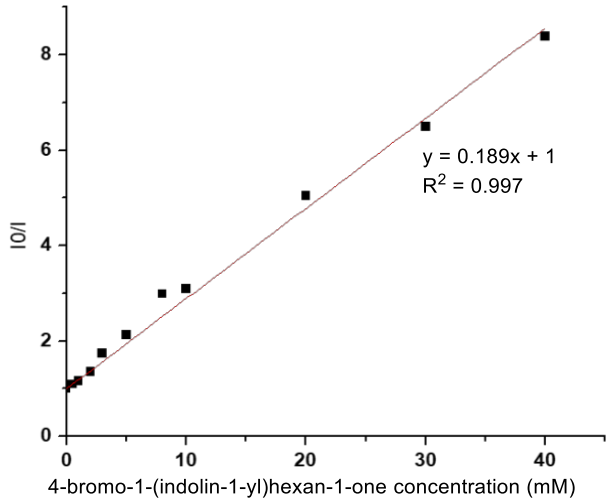


Figure S7. Plot of I_0/I versus the concentration of 4-bromo-1-(indolin-1-yl)hexan-1-one for (**P**Cu^{I}(OPh).

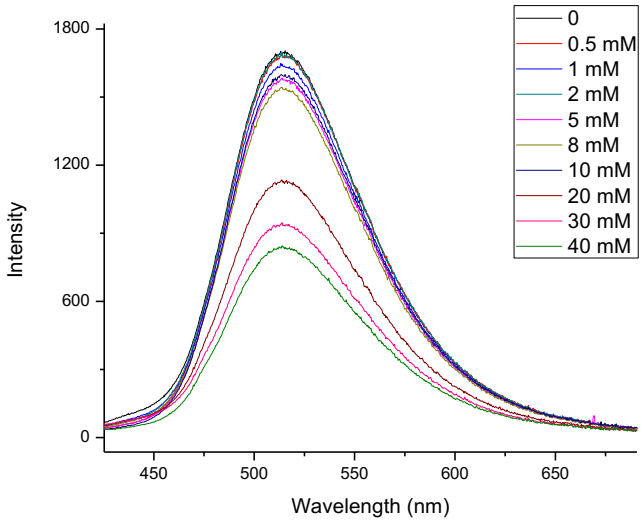


Figure S8. Emission spectra of **P**Cu^{I}(amidate) upon irradiation at 400 nm in the presence of varying amounts of 4-bromo-1-(indolin-1-yl)hexan-1-one.

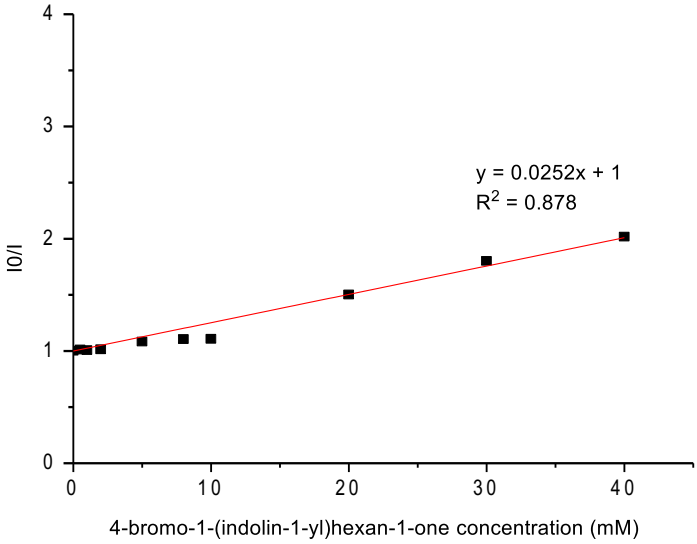


Figure S9. Plot of I_0/I versus the concentration of 4-bromo-1-(indolin-1-yl)hexan-1-one for (**P**Cu^{I}(amidate).

Estimated excited-state reduction potentials of PCu^{I}(OPh) and PCu^{I}(amidate). In order to measure the estimated excited-state reduction potentials of **P**Cu^{I}(OPh) and **P**Cu^{I}(amidate), their ground-state reduction potentials were first measured. In a glovebox, a solution of **P**Cu^{I}(OPh) (1.0 mM, 6.0 mg) or **P**Cu^{I}(amidate) (1.0 mM, 6.5 mg) and NBu_4PF_6 (0.20 M, 388 mg, as electrolyte) in THF (5.0 mL) was prepared. A reference solution of AgOTf (5.0 mM, 6.4 mg) and NBu_4PF_6 (0.20 M, 388 mg, as electrolyte) in THF (5.0 mL) was also prepared. The estimated ground-state reduction potentials of **P**Cu^{I}(OPh) and **P**Cu^{I}(amidate) complexes were then measured by cyclic voltammetry (CV) studies, which were determined to be $E^0_{1/2}$ ($Cu^{II/I}$) = 0.0 V vs Fc^+/Fc for **P**Cu^{I}(OPh) and $E^0_{1/2}$ ($Cu^{II/I}$) = 0.5 V vs Fc^+/Fc for **P**Cu^{I}(amidate).

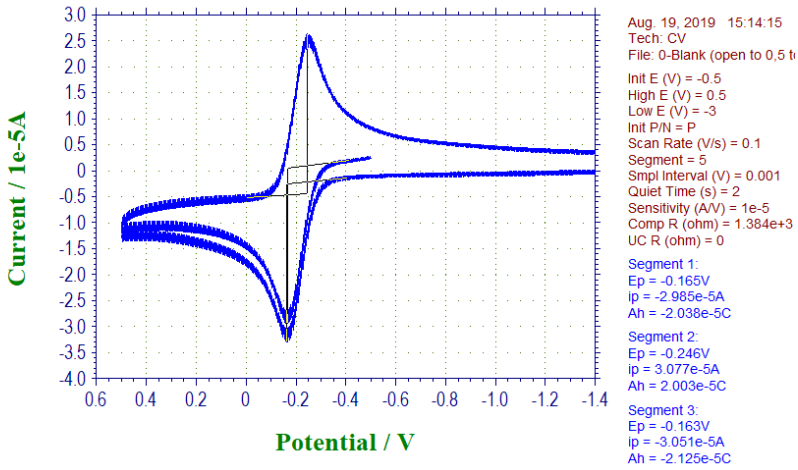
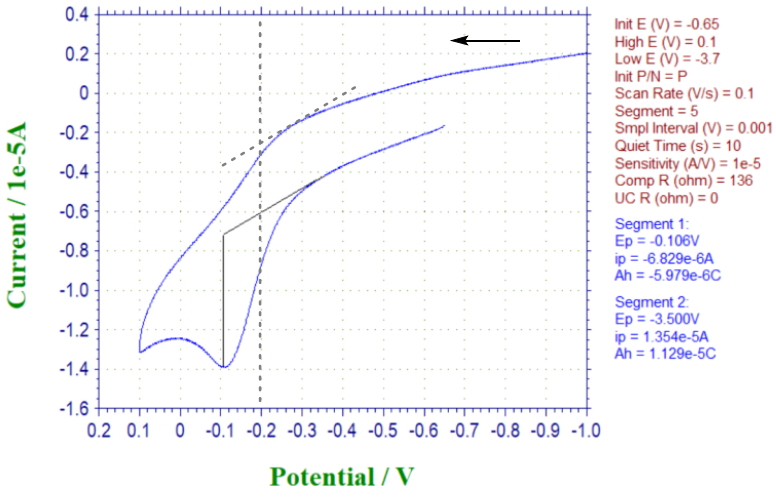


Figure S10. Cyclic voltammetry of ferrocenium (half-wave redox potential $E^0_{1/2}$ (Fc^+/Fc) = –0.2 V).



Estimated half wave redox potential

$E^0_{1/2}$ ($Cu^{II/I}$) vs Fc^+/Fc = -0.2 + 0.2 = 0.0 V

Figure S11. Cyclic voltammetry of **P**Cu^{I}(OPh).

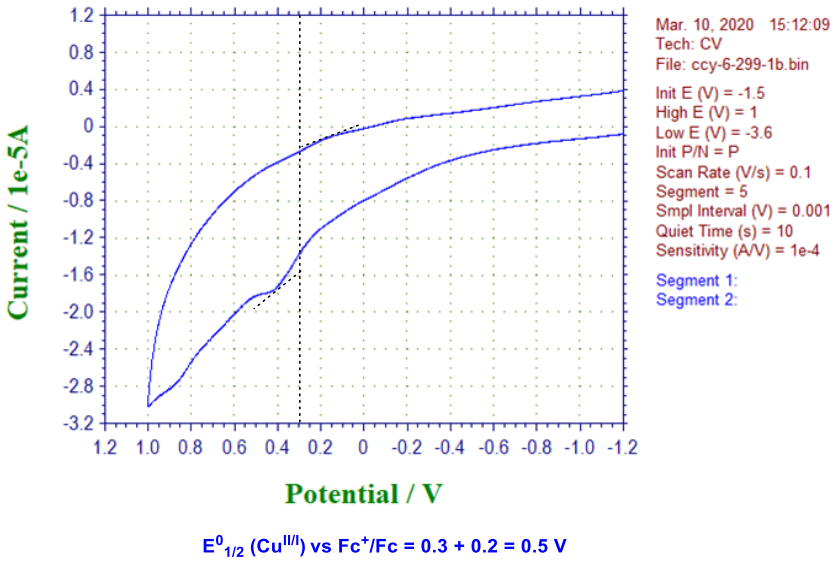


Figure S12. Cyclic voltammetry of **P**Cu^{I}(amidate).

Excitation and emission spectra of PCu^{I}(OPh) and PCu^{I}(amidate). In a glovebox, a solution of **P**Cu^{I}(OPh) (0.83 mM, 3.0 mg) or **P**Cu^{I}(amidate) (0.83 mM, 3.3 mg) in 2-Me-THF (3.0 mL) was prepared in a 4 mL cuvette. The excitation and emission spectra were then measured by steady-state fluorescence spectroscopy.

Estimated excited-state reduction potential for PCu^{I}(OPh). The overlap of the excitation and emission spectra occurred at 438 nm, which corresponds to an energy of 2.8 eV. Together with the ground-state reduction potential ($E^{0}_{1/2}$ ($Cu^{II/I}$) = 0.0 V vs Fc^{+}/Fc), the excited-state reduction potential of **P**Cu^{I}(OPh) complex is estimated to be E* ($Cu^{II/I*}$) vs Fc^{+}/Fc = –2.8 V.

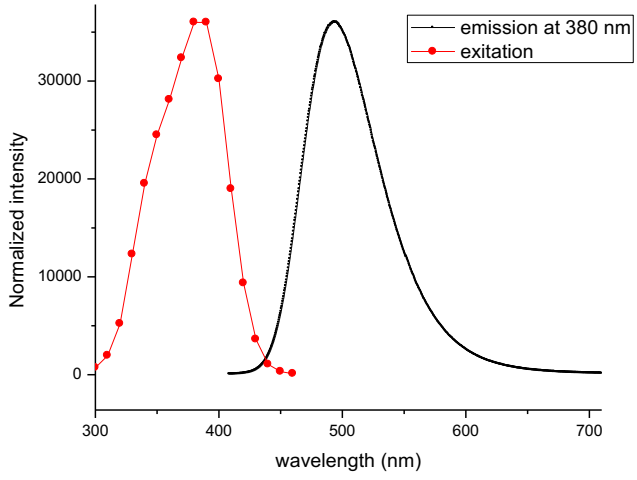


Figure S13. Excitation and emission spectra of **P**Cu^{I}(OPh) (overlap at 438 nm).

Estimated excited-state reduction potential for PCu^{I}(amidate). The overlap of the excitation and emission spectra occurred at 446 nm, which corresponds to an energy of 2.8 eV. Together with the ground-state reduction potential ($E^{0}_{1/2}$ ($Cu^{II/I}$) = 0.5 V vs Fc^{+}/Fc), the excited-state reduction potential of **P**Cu^{I}(amidate) complex is estimated to be E* ($Cu^{II/I*}$) vs Fc^{+}/Fc = –2.3 V.

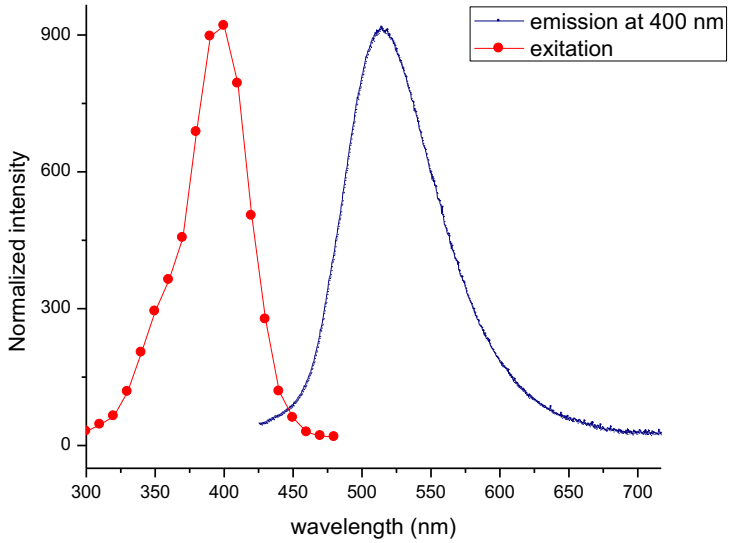
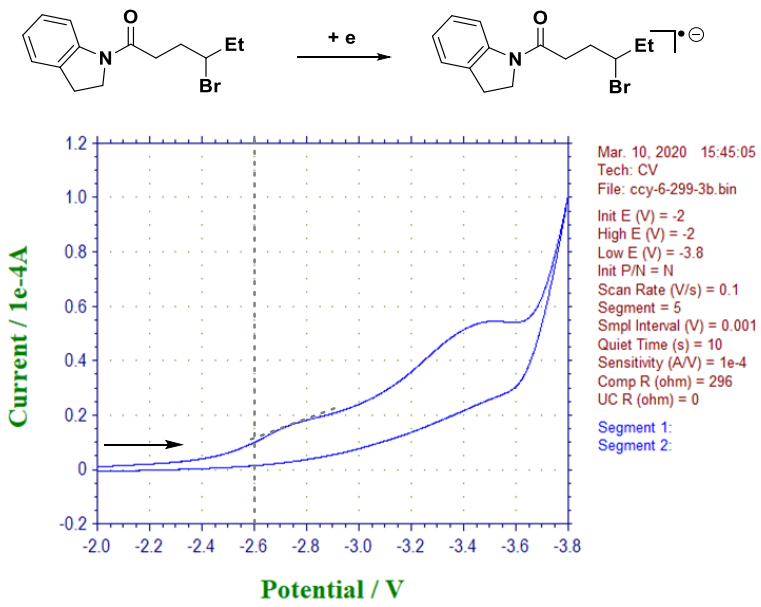


Figure S14. Excitation and emission spectra of **P**Cu^{I}(amidate) (overlap at 446 nm).

Reduction potentials of the electrophiles. In a glovebox, solutions of 4-bromo-1-(indolin-1-yl)hexan-1-one (2.0 mM, 3.0 mg) and diethyl (3-bromopentyl)phosphonate (2.0 mM, 2.9 mg), with NBu_4PF_6 (0.20 M, 388 mg) as electrolyte, in THF (5.0 mL) were prepared. A reference solution comprised of AgOTf (5.0 mM, 6.4 mg) and NBu_4PF_6 (0.20 M, 388 mg, as electrolyte) in THF (5.0 mL) was also prepared. The reduction potentials ($RX/RX^{\bullet -}$) of 4-bromo-1-(indolin-1-yl)hexan-1-one and diethyl (3-bromopentyl)phosphonate were then measured by cyclic voltammetry (CV).

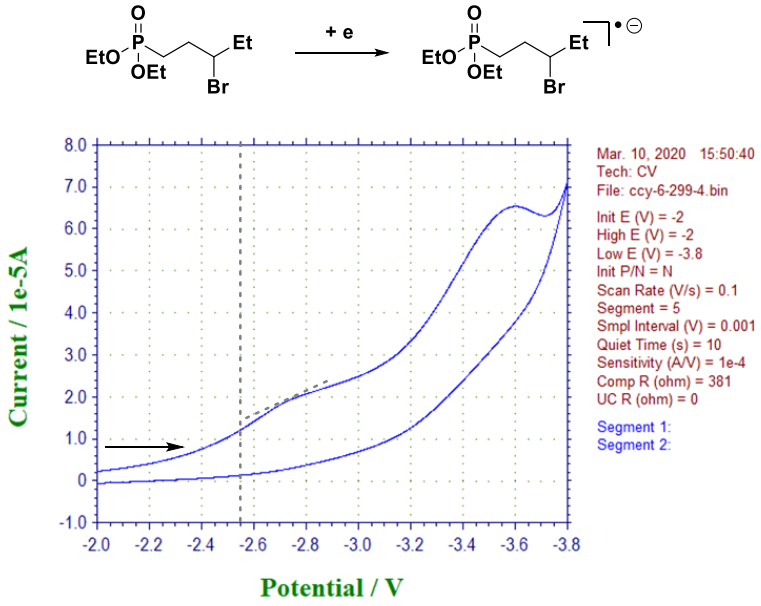
Because the CV of the electrophiles are irreversible, half-peak potentials[15] are reported herein. The half-peak reduction potentials ($E_{p/2}$) of 4-bromo-1-(indolin-1-yl)hexan-1-one and diethyl (3-bromopentyl)phosphonate were determined to be –2.4 V and –2.3 V vs Fc^{+}/Fc, respectively.



Estimated half-peak redox potential

$E_{p/2}$ (vs Fc^+/Fc) = -2.6 + 0.2 = -2.4 V

Figure S15. CV of 4-bromo-1-(indolin-1-yl)hexan-1-one ($E_{p/2}$ = –2.4 V vs Fc^+/Fc).



Estimated half-peak redox potential

$E_{p/2}$ (vs Fc^+/Fc) = -2.5 + 0.2 = -2.3 V

Figure S16. CV of diethyl (3-bromopentyl)phosphonate ($E_{p/2}$ = –2.3 V vs Fc^+/Fc).

Identification of the photocatalyst. In order to determine whether **P**Cu^I(OPh) or **P**Cu^I(amidate) is the photocatalyst, ^{19}F NMR analysis of the catalysis system was conducted

using both *i*-Pr$_2$O and 2-Me-THF as solvent. The ^{19}F NMR spectra revealed that there is no appreciable amount of **P**Cu^{I}(amidate) in the catalysis system either in *i*-Pr$_2$O or in 2-Me-THF.

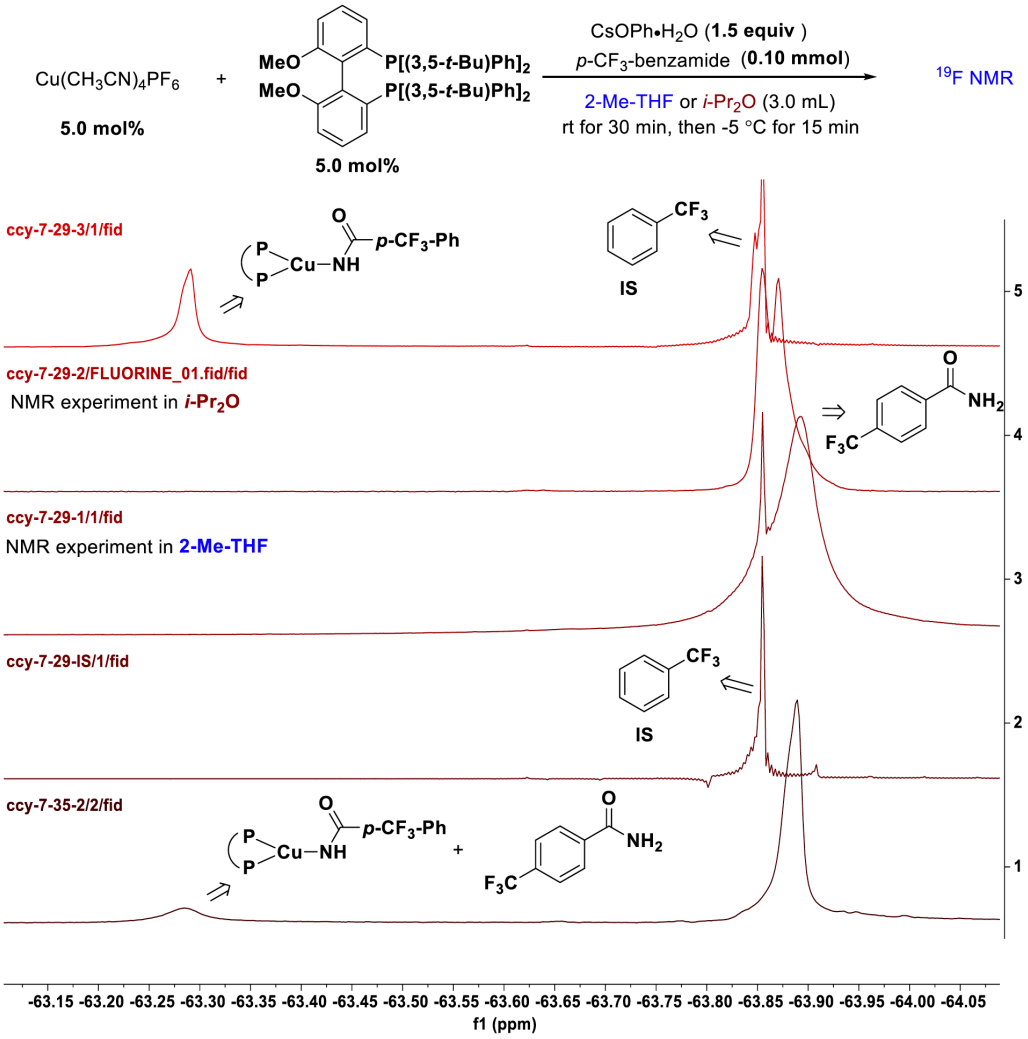


Figure S17. ^{19}F NMR analysis of the catalysis system.

In order to further confirm that there is no appreciable amount of **P**Cu^{I}(amidate) in the catalysis system, a titration experiment was conducted in 2-Me-THF. When 3.0 equiv of *p*-CF$_3$-benzamide was added to a solution of **P**Cu^{I}(OPh) in 2-Me-THF, no **P**Cu^{I}(amidate) complex was generated as determined by ^{19}F NMR. On the other hand, when 3.0 equiv of phenol was added to a solution of **P**Cu^{I}(amidate) in 2-Me-THF, all of the **P**Cu^{I}(amidate) was converted to **P**Cu^{I}(OPh).

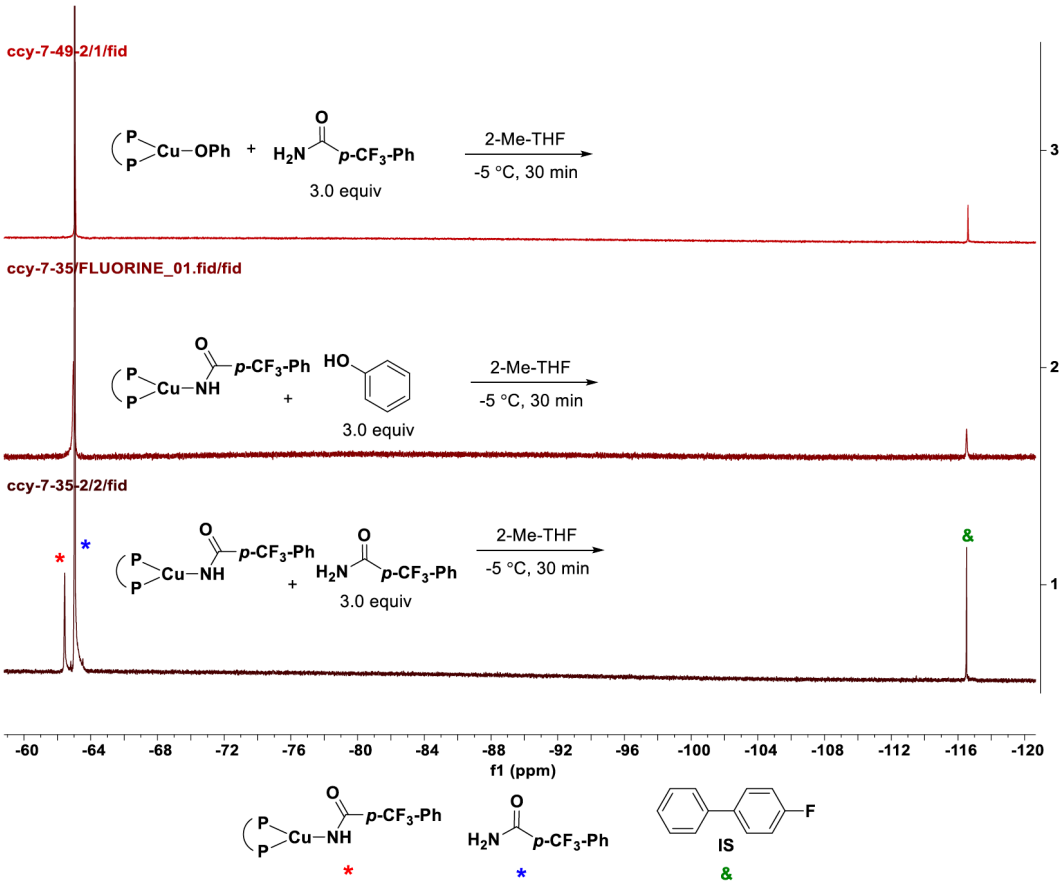


Figure S18. ^{19}F NMR spectra of titration experiments in 2-Me-THF.

The titration experiment was also conducted in d$_8$-THF. When 1.0 equiv or 3.0 equiv of *p*-CF$_3$-benzamide was added to a solution of **P**Cu^{I}(OPh) complex in d$_8$-THF, no **P**Cu^{I}(amidate) complex was generated as determined by ^{1}H NMR. On the other hand, when 1.0 equiv or 3.0 equiv of phenol was added to a solution of **P**Cu^{I}(amidate) in d$_8$-THF, all of the **P**Cu^{I}(amidate) was converted to **P**Cu^{I}(OPh).

Our NMR experiments indicate that there is no appreciable amount of **P**Cu^{I}(amidate) in the catalytic reaction, and that **P**Cu^{I}(amidate) can be fully converted into **P**Cu^{I}(OPh) in the presence of phenol.

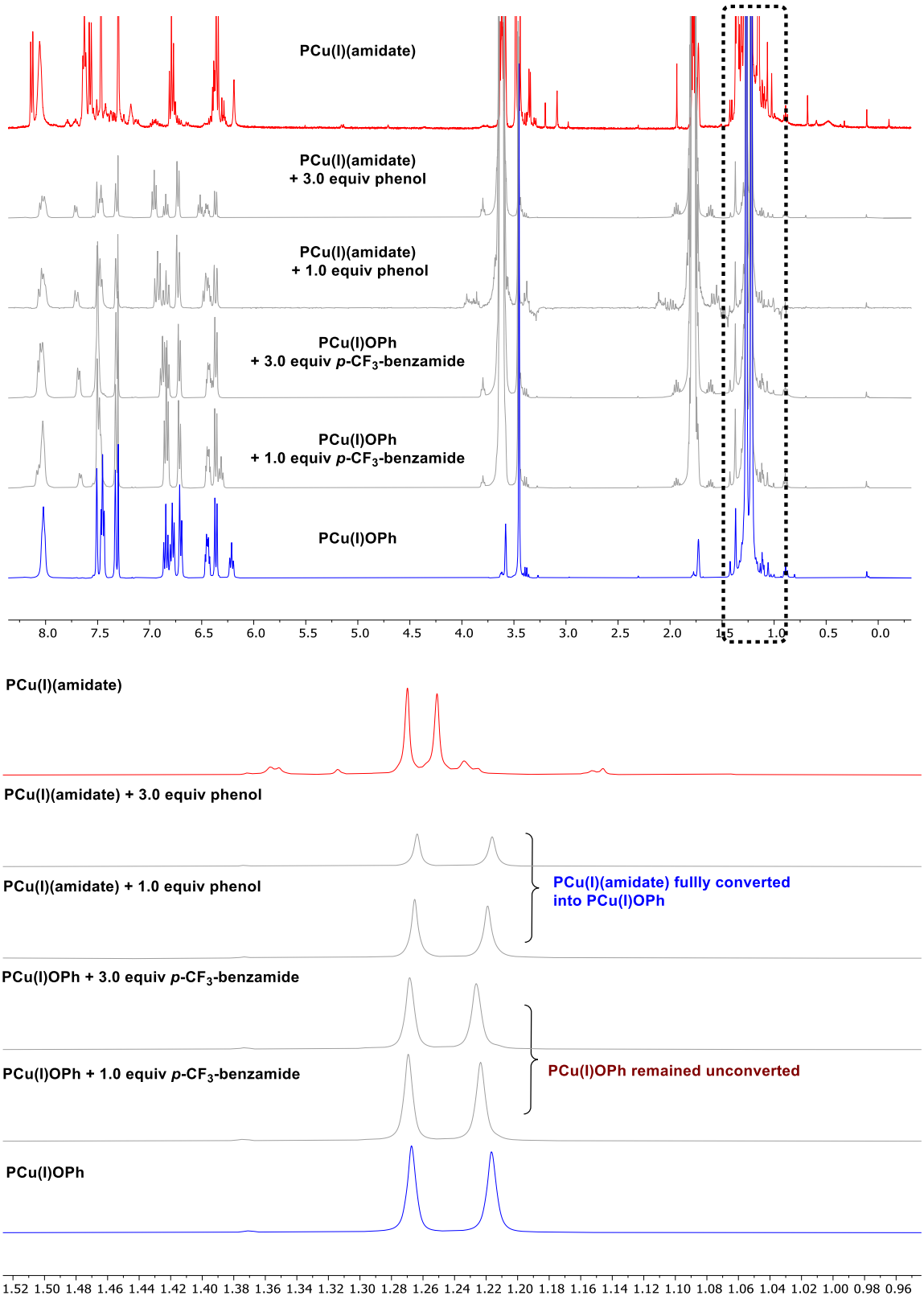


Figure S19. ^{1}H NMR spectra of titration experiments in d$_8$-THF.

Estimation of the amount of photocatalyst PCu^{I}(OPh) in a catalytic reaction. The catalytic reaction was set up following **GP-11** on a 0.10 mmol scale. After 4 h, the reaction vial was removed from the cryocool and immersed in liquid nitrogen for 5 min. The vial was then taken quickly into a glovebox and placed in the cold well in the glovebox. An internal standard (diethyl (3-bromopentyl)phosphonate, 10.2 mg, 0.035 mmol) was added, and then an aliquot of the reaction mixture (0.50 mL) was quickly filtered into a J-Young NMR tube. The J-Young NMR tube was then quickly taken out of the glovebox and immersed in liquid nitrogen. The sample was then analyzed quickly by ^{31}P NMR spectroscopy at –5 °C. ^{31}P NMR analysis revealed the presence of ~3.9 mol% **P**Cu^{I}(OPh) (~33% of all the copper catalyst).

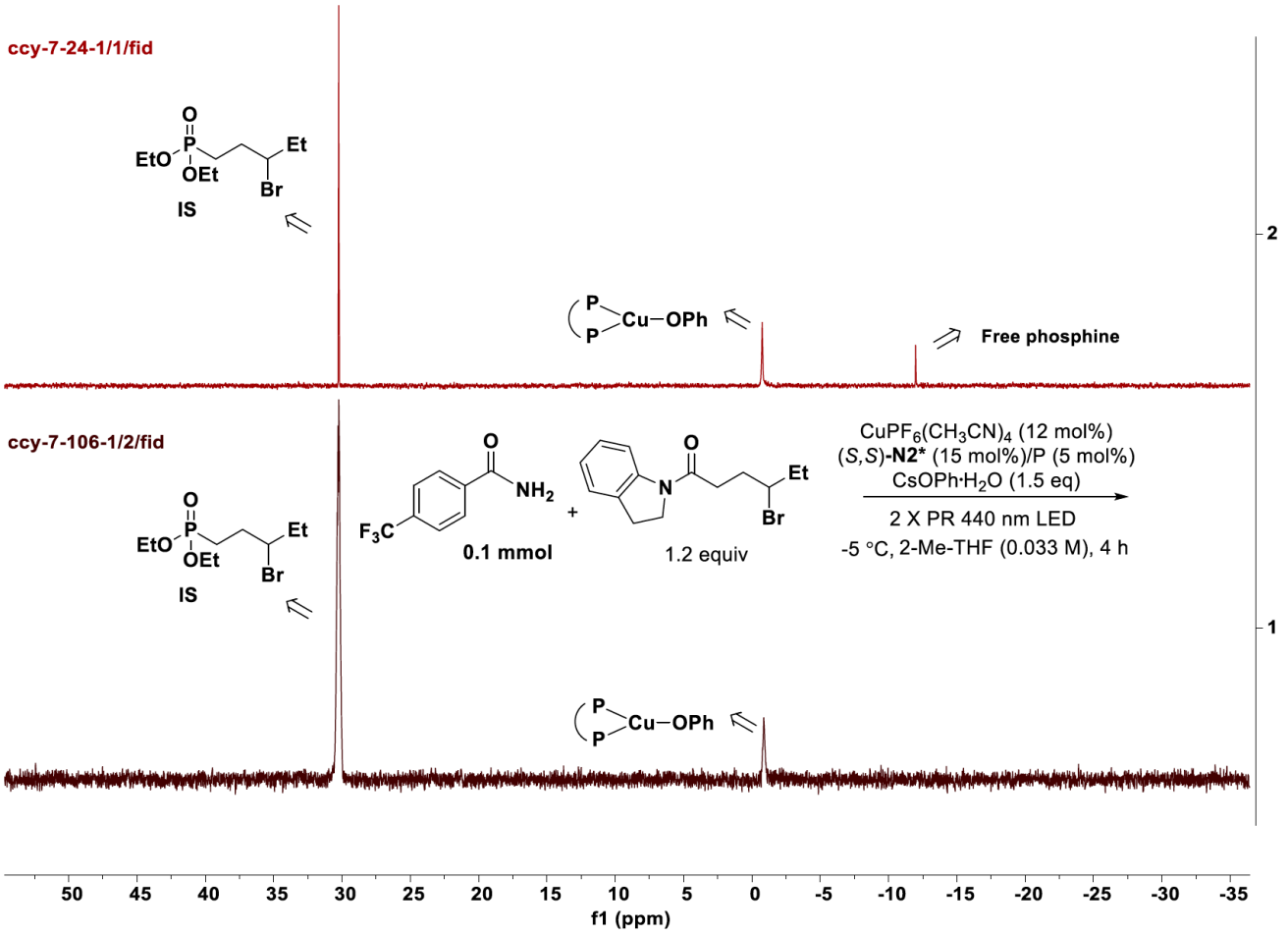


Figure S20. ^{31}P NMR spectrum of a catalytic reaction at 4 h.

Overlap between the emission of the blue LED lamp and the absorption of PCu^{I}(OPh). In a glovebox, a solution of **P**Cu^{I}(OPh) (0.050 mM, 3.0 mL) was prepared in a 4 mL cuvette. The absorption spectrum of **P**Cu^{I}(OPh) was then measured with a UV-Vis spectrophotometer.

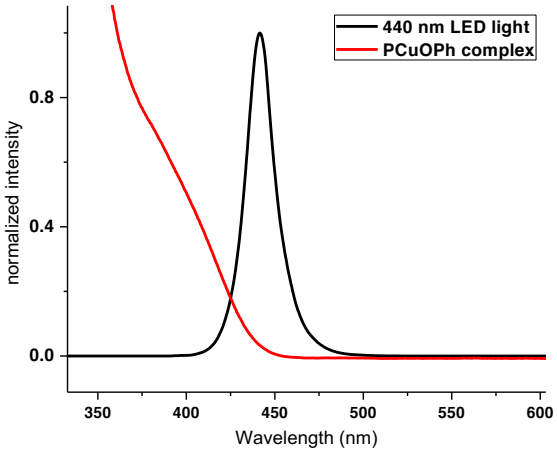


Figure S21. Overlap between the emission of the blue LED lamp and the absorption of **P**Cu^{I}(OPh).

EPR study of the catalysis system. In a glovebox, a suspension of $Cu(CH_3CN)_4PF_6$ (4.5 mg, 0.012 mmol, 12 mol%), *rac*-**P** (5.2 mg, 0.0050 mmol, 5.0 mol%), (*S*,*S*)-**N2*** (3.6 mg, 0.015 mmol, 15 mol%), and $CsOPh·H_2O$ (36.6 mg, 0.15 mmol, 1.5 equiv) in anhydrous 2-Me-THF (3.0 mL) in a 4 mL vial was stirred at room temperature for 30 min. Next, 4-CF_3-benzamide (18.9 mg, 0.10 mmol, 1.0 equiv) or ^{15}N labeled 4-CF_3-benzamide (19.0 mg, 0.10 mmol, 1.0 equiv, prepared following **GP-9** from $^{15}NH_4Cl$) was weighed into the vial, and then 4-bromo-1-(indolin-1-yl)hexan-1-one (35.5 mg, 0.12 mmol, 1.2 equiv) was added. The 4 mL vial was sealed with a polypropylene screw cap, transferred out of the glovebox, placed in a cryocool with a well-stirred isopropanol bath precooled to −5 °C, and fixed upside down with a copper wire holder. The reaction mixture was stirred at −5 °C for 5 min, and then it was irradiated with two PR 440 nm Kessil blue LED lamps, placed ~5 cm away, for 4 h. The vial was then taken out of the cryocool, frozen with liquid nitrogen, transferred into the glovebox, and placed in the cold well (–78 °C) in the glovebox. The reaction suspension was filtered quickly using a syringe filter and transferred into an EPR tube (frozen with liquid nitrogen) for X-band EPR or Q-band ENDOR and HYSCORE measurements.

Upon integration of the EPR spectrum ($CuSO_4•5H_2O$ was used for calibration), the amount of Cu(II) species was estimated to be ~5.0 mol% (~42% of all the copper catalyst) at a reaction time of 4 h.

To reveal whether **N2***Cu^{II}(amidate)X is responsible for the observed EPR signals of the catalytic reaction, Q-band ENDOR and HYSCORE experiments of the catalytic reaction were conducted with both ^{14}N and ^{15}N *p*-CF_3-benzamide at 4 h (Figure S23 and Figure S25). The ENDOR and HYSCORE of the reaction with ^{15}N *p*-CF_3-benzamide show no obvious ^{15}N signals, and are identical with those of ^{14}N *p*-CF_3-benzamide. These results suggest that the Cu(II) species observed by EPR do not contain an appreciable amount of **N2***Cu^{II}(amidate)X species. Moreover, the X-band CW EPR (Figure S22) and Q-band field sweep data (Figure S24) are identical with ^{14}N and ^{15}N *p*-CF_3-benzamide, which further support this conclusion.

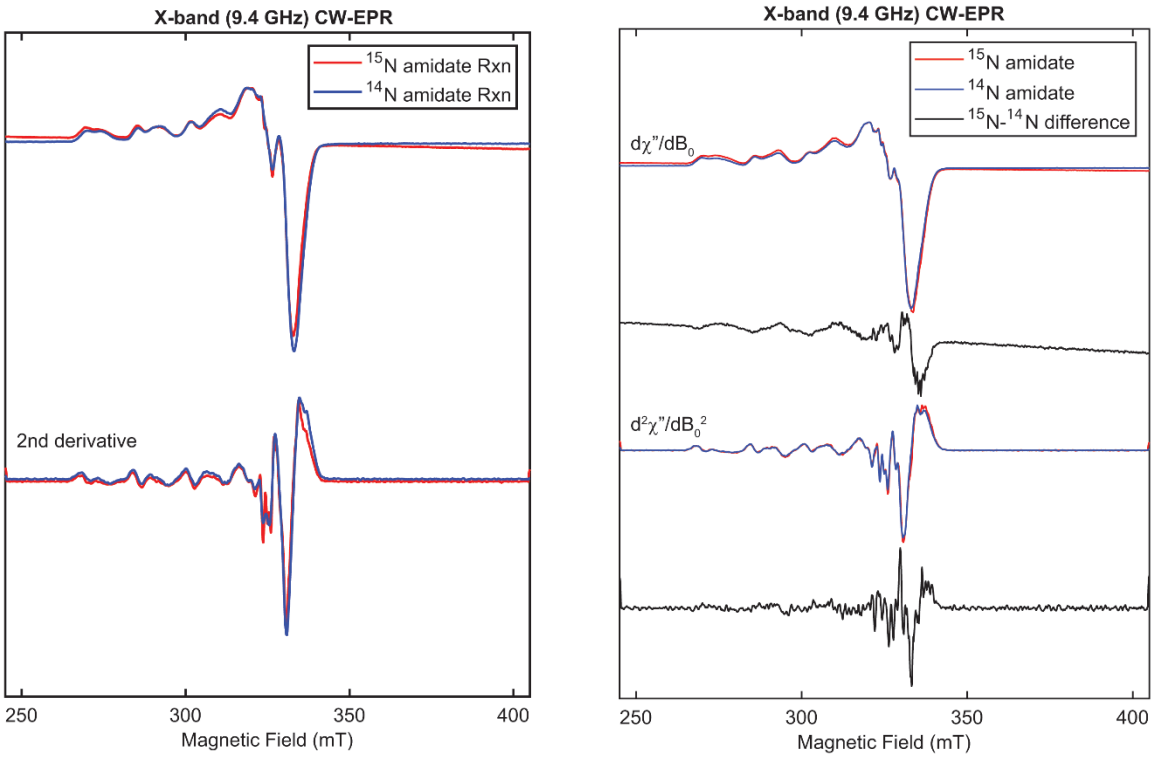


Figure S22. X-band EPR spectra of the catalytic reaction at 4 h (9.4 GHz, 77 K).

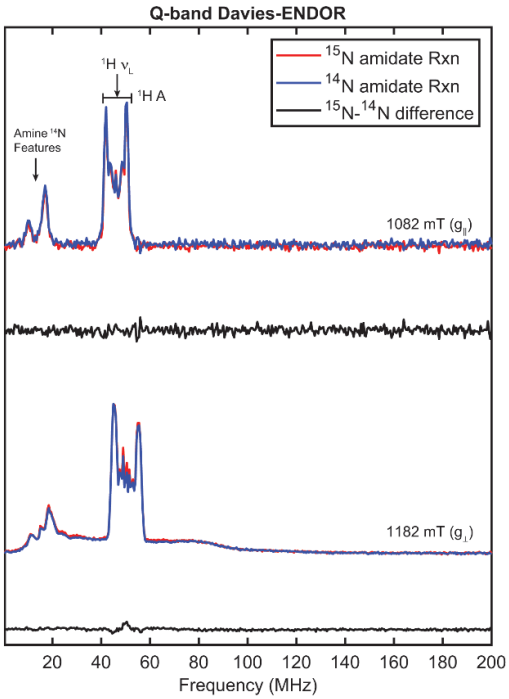


Figure S23. Q-band ENDOR of the catalytic reaction at 4 h

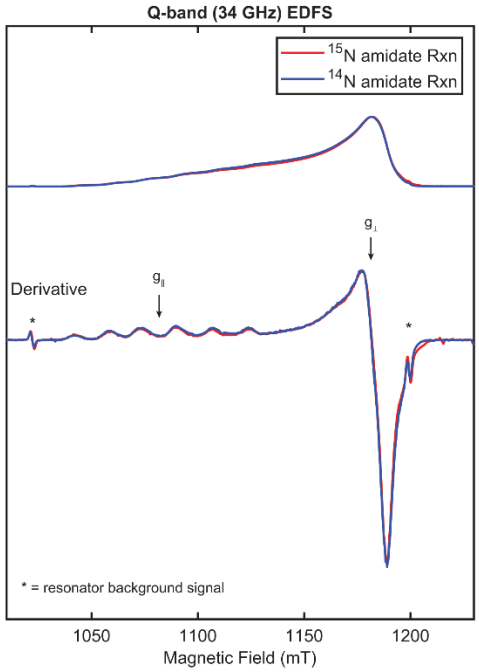


Figure S24. Q-band echo-detected field sweeps (EDFS) of the catalytic reaction at 4 h.

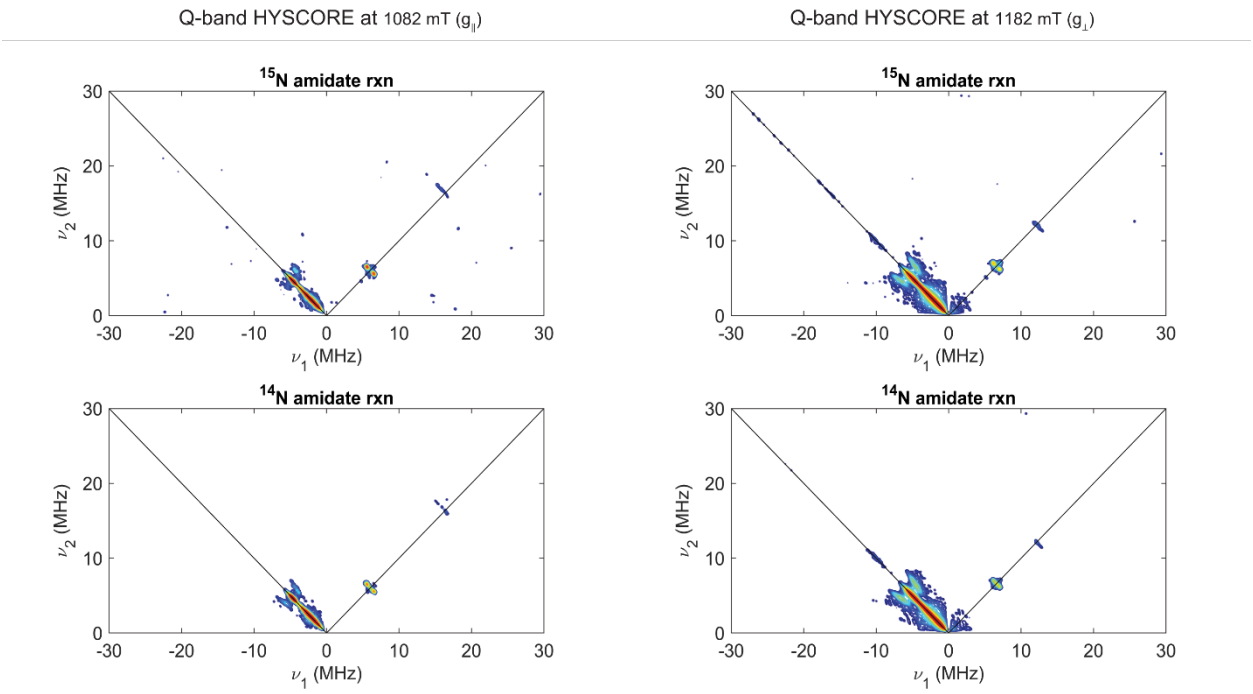


Figure S25. Q-band HYSCORE of the catalytic reaction at 4 h.

EPR analysis of N2*Cu^{II}(OPh)$_2$ prepared independently. In a glovebox, a suspension of $CuCl_2$ (1.6 mg, 0.012 mmol) and (*S*,*S*)-**N2*** (2.9 mg, 0.012 mmol, 1.0 equiv) in 2-Me-THF (1.5 mL) in a 4 mL vial was stirred for 30 min. The vial was then taken out of the glovebox and cooled to –5 °C in a cryocool. A solution of NaOPh (2.8 mg, 0.024 mmol, 2.0 equiv) in 2-Me-THF (1.5 mL) was then added slowly. The resulting suspension was stirred for 5 min. The vial was then taken out of the cryocool, frozen with liquid nitrogen, transferred into the glovebox, and placed in the cold well (–78 °C) in the glovebox. The reaction suspension was filtered quickly using a syringe filter and transferred into an EPR tube (frozen with liquid nitrogen) for X-band EPR measurement at 77 K.

EPR analysis of N2*Cu^{II}(OPh)Br prepared independently. In a glovebox, a suspension of $CuBr_2$ (2.7 mg, 0.012 mmol) and (*S*,*S*)-**N2*** (2.9 mg, 0.012 mmol, 1.0 equiv) in 2-Me-THF (1.5 mL) in a 4 mL vial was stirred for 30 min. The vial was then taken out of the glovebox and cooled to –5 °C in a cryocool. A solution of NaOPh (1.4 mg, 0.012 mmol, 1.0 equiv) in 2-Me-THF (1.5 mL) was then added slowly. The resulting suspension was stirred for 2 min. The vial was then taken out of the cryocool, frozen with liquid nitrogen, transferred into the glovebox, and placed in the cold well (–78 °C) in the glovebox. The reaction suspension was filtered quickly using a syringe filter and transferred into an EPR tube (frozen with liquid nitrogen) for X-band EPR measurement at 77 K.

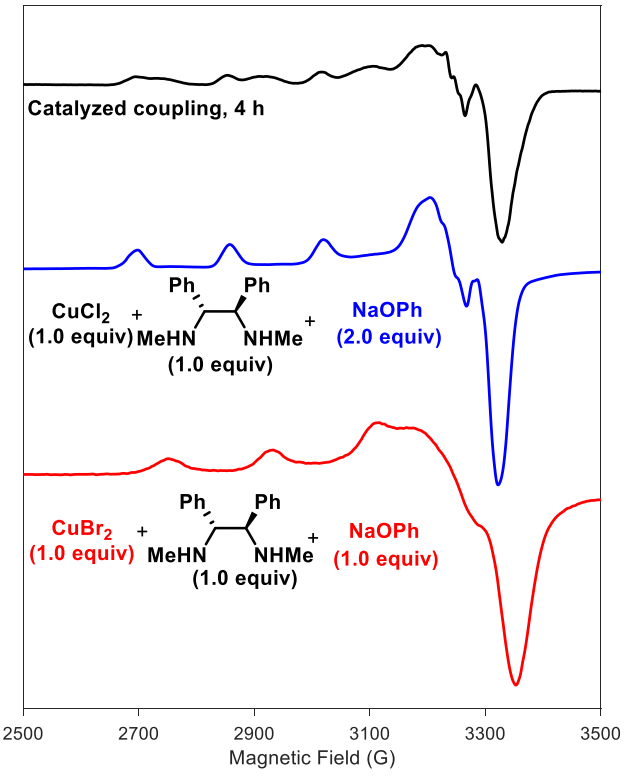


Figure S26. X-band EPR spectra of complexes prepared in situ (9.4 GHz, 77 K).

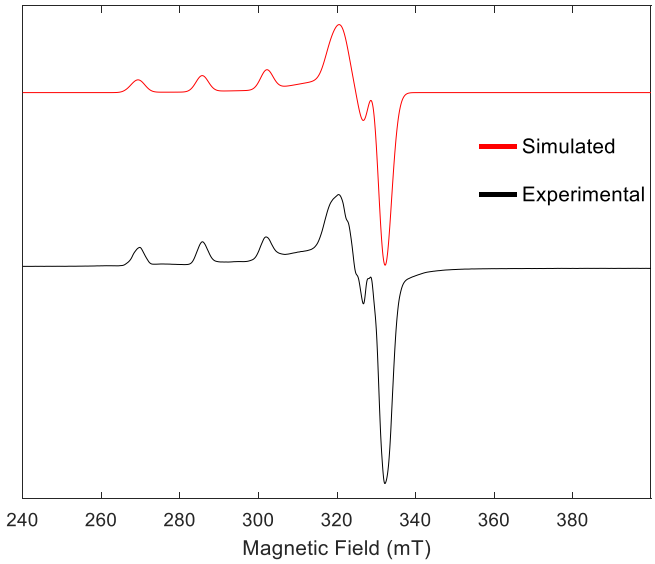


Figure S27. Simulation of **N2***$Cu^{II}(OPh)_2$ prepared in situ.

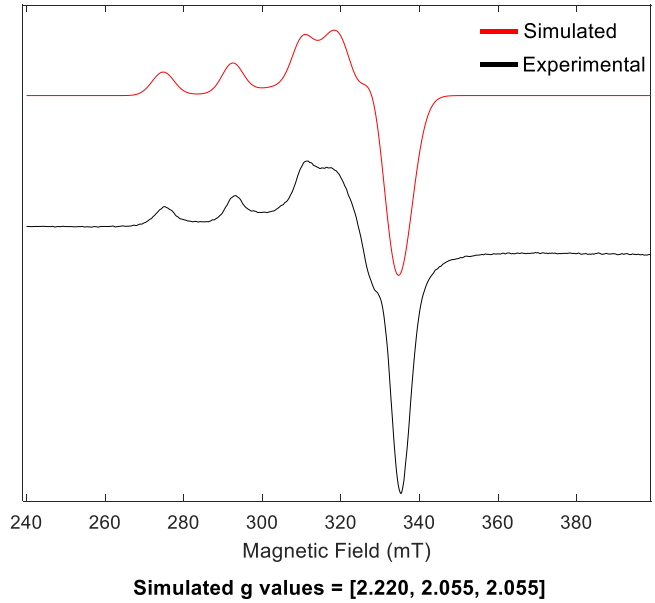


Figure S28. Simulation of **N2***$Cu^{II}(OPh)Br$ prepared in situ.

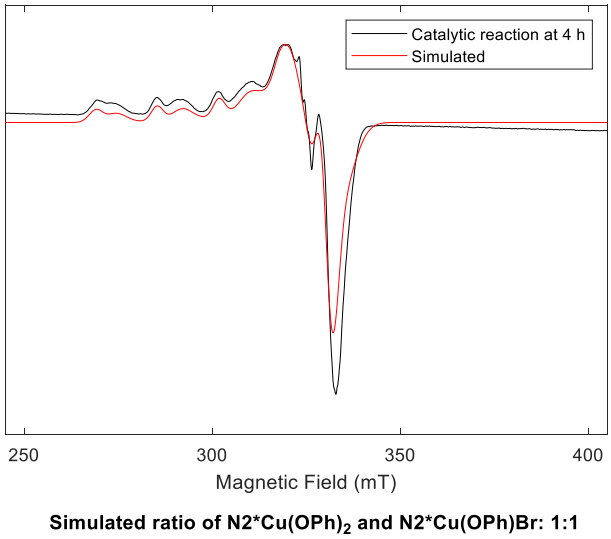


Figure S29. Simulation of the catalytic reaction at 4 h.

EPR study: Reaction with Magic Blue (tris(4-bromophenyl)ammoniumyl hexachloroantimonate). In a glovebox, a solution of **P**Cu^{I}(OPh) (6.6 mg, 0.0050 mmol), (*S,S*)-**N2*** (1.2 mg, 0.0050 mmol, 1.0 equiv), and NaOPh (5.8 mg, 0.050 mmol, 10 equiv) in 2-Me-THF (0.5 mL) in a 4.0 mL vial was stirred for 1 min at room temperature. To the solution was added Magic Blue (4.1 mg, 0.0050 mmol, 1.0 equiv), and the resulting suspension was stirred for 2 min at room temperature. The mixture was quickly transferred into an EPR tube (frozen with liquid nitrogen) for X-band EPR measurement at 77 K.

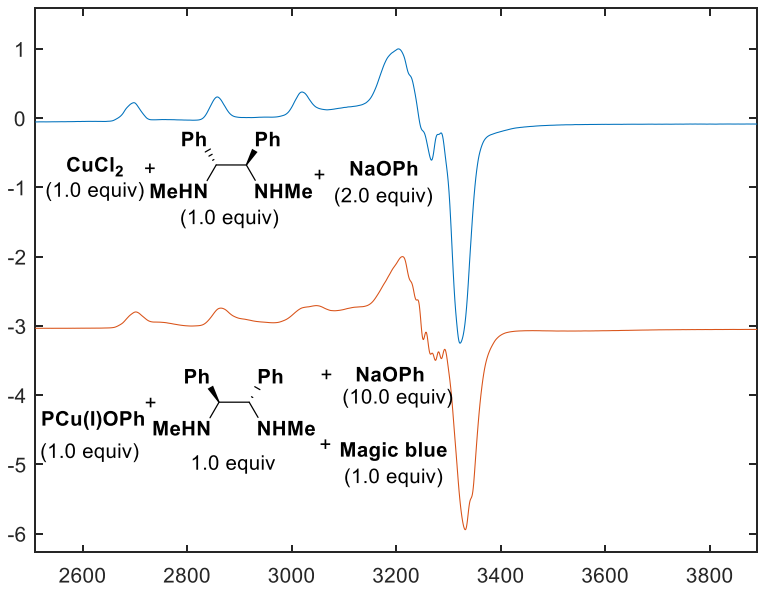


Figure S30. X-band EPR spectra: Reaction with Magic Blue versus **N2***Cu^{II}(OPh)$_2$ prepared in situ.

Monitoring the catalytic system via ESI mass spectrometry. In a glovebox, a suspension of $Cu(CH_3CN)_4PF_6$ (4.5 mg, 0.012 mmol, 12 mol%), *rac*-**P** (5.2 mg, 0.0050 mmol, 5.0 mol%), (*S*,*S*)-**N2*** (3.6 mg, 0.015 mmol, 15 mol%), and $CsOPh·H_2O$ (36.6 mg, 0.15 mmol, 1.5 equiv) in anhydrous 2-Me-THF (3 mL) in a 4 mL vial was stirred at room temperature for 30 min. Next, 4-CF_3-benzamide (18.9 mg, 0.10 mmol, 1.0 equiv) was weighed into the vial, and then 4-bromo-1-(indolin-1-yl)hexan-1-one (0.12 mmol, 1.2 equiv) was added. The 4 mL vial was sealed with a polypropylene screw cap, transferred out of the glovebox, placed into a cryocool with a well-stirred isopropanol bath precooled to −5 °C, and fixed upside down with a copper wire holder. The reaction mixture was stirred at −5 °C for 5 min, and then it was irradiated with two PR 440 nm Kessil blue LED lamps, placed ~5 cm away, for 4 h. The vial was then taken out of the cryocool, frozen with liquid nitrogen, transferred into the glovebox, and placed in the cold well (–78 °C) in the glovebox. The reaction suspension was filtered quickly using a syringe filter and subjected to ESI mass analysis quickly.

The ESI mass spectrometry confirmed the presence of **N2***$Cu^{II}(OPh)_2$.

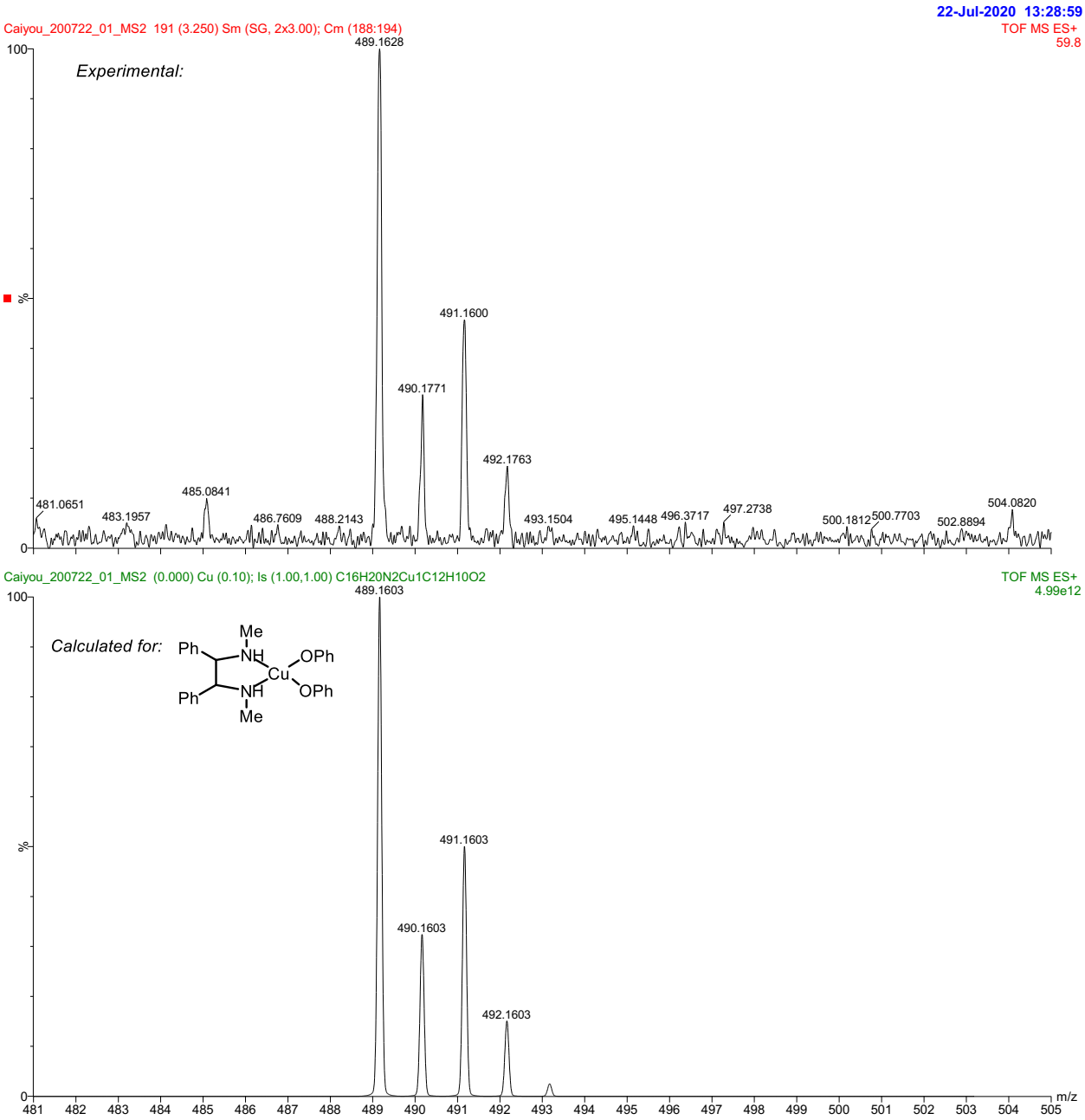


Figure S31. Experimental and calculated ESI mass spectrum of **N2***$Cu^{II}(OPh)_2$.

TEMPO trapping experiment (Fig. 4e). In a glovebox, a suspension of $Cu(CH_3CN)_4PF_6$ (4.5 mg, 0.012 mmol, 12 mol%), *rac*-**P** (5.2 mg, 0.0050 mmol, 5.0 mol%), (*S*,*S*)-**N2*** (3.6 mg, 0.015 mmol, 15 mol%), and CsOPh·H_2O (36.6 mg, 0.15 mmol, 1.5 equiv) in anhydrous 2-Me-THF (3.0 mL) in a 4 mL vial was stirred at room temperature for 30 min. Next, 4-CF_3-benzamide (18.9 mg, 0.10 mmol, 1.0 equiv) was weighed into the vial, and then 4-bromo-1-(indolin-1-yl)hexan-1-one (35.5 mg, 0.12 mmol, 1.2 equiv) and TEMPO (7.8 mg, 0.050 mmol, 50 mol%) were added. The vial was sealed with a polypropylene screw cap, transferred out of the glovebox, placed into a cryocool with a well-stirred isopropanol bath precooled to −5 °C, and fixed upside down with a copper wire holder. The reaction mixture was stirred at −5 °C for 5 min, and then it was irradiated with two PR 440 nm Kessil blue LED lamps, placed ~5 cm away, for 24 h. The resulting solution was then concentrated and the residue was purified by preparative TLC.

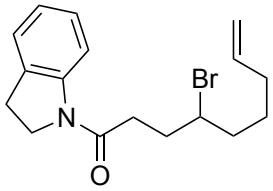
^{1}H NMR (500 MHz, C_6D_6) δ 8.70 (d, *J* = 8.1 Hz, 1H), 7.03 (t, *J* = 7.7 Hz, 1H), 6.87 (d, *J* = 7.3 Hz, 1H), 6.81 (t, *J* = 7.3 Hz, 1H), 4.41 (dd, *J* = 9.8, 4.6 Hz, 1H), 4.15 (td, *J* = 10.2, 6.6 Hz, 1H), 3.61 (td, *J* = 10.2, 6.9 Hz, 1H), 2.67 – 2.51 (m, 2H), 2.14 – 2.01 (m, 1H), 1.88 – 1.80 (m, 1H), 1.38 – 1.02 (m, 22H), 0.83 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, C_6D_6) δ 170.7, 143.3, 131.3, 127.6, 124.2, 123.6, 117.9, 85.1, 60.4, 59.3, 47.9, 40.4, 40.2, 33.3, 33.0, 31.4, 31.2, 27.8, 24.9, 20.2, 19.9, 17.0, 9.4.

FT-IR (film) 2932, 2362, 1650, 1600, 1482, 1462, 1412, 1261, 1132, 1016, 753 cm^{-1}.HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{23}H_{36}N_2O_2$: 373.2850, found: 373.2845.

m.p.: 107-108 °C.

TEMPO trapping experiment: Control reaction. Following the procedure of the TEMPO trapping experiment above, TEMPO–Na (50 mol%) was used as an additive instead of TEMPO, and the reaction was conducted without light. No (<1%) TEMPO adduct was observed (two runs).



4-Bromo-1-(indolin-1-yl)non-8-en-1-one. Anhydrous CH_2Cl_2 (150 mL) and oxalyl chloride (4.2 mL, 50 mmol, 1.3 equiv) were added to an oven-dried round-bottom flask under nitrogen. The solution was cooled to 0 °C, and 4-oxonon-8-enoic acid (6.34 g, 37.3 mmol, 1.0 equiv, synthesized according to a literature procedure[16]) was added. Next, DMF (0.3 mL, 3.7 mmol, 0.10 equiv) was added dropwise, and the reaction was monitored at 0 °C for 2 h, at which time gas evolution ended. The reaction mixture was concentrated to remove the excess oxalyl chloride and CH_2Cl_2. The residue was then dissolved in dry CH_2Cl_2 (150 mL) under a nitrogen atmosphere. The resulting solution was cooled to 0 °C, and indoline (5.34 g, 44.8 mmol, 1.1 equiv) was added slowly, followed by the addition of triethylamine (7.53 g, 74.6 mmol, 2.0 equiv). The resulting suspension was allowed to warm to room temperature and stir for 1 h.

Water (80 mL) was added to quench the reaction, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (80 mL x 2), and the organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated. The residue was then purified by flash column chromatography on silica gel (25% EtOAc/hexane) to afford 1-(indolin-1-yl)non-8-ene-1,4-dione. White solid. 4.30 g, 43% yield.

To a 0 °C solution of 1-(indolin-1-yl)non-8-ene-1,4-dione (4.30 g, 15.8 mmol, 1.0 equiv) in MeOH (100 mL) was slowly added a solution of $NaBH_4$ (1.19 g, 31.6 mmol, 2.0 equiv) in MeOH (20 ml) and 1 wt% aqueous NaOH (1.0 mL). The solution was allowed to warm to room temperature and stir for 1 h. The reaction was then quenched via the slow addition of 1 N aqueous HCl (20 mL). After removing MeOH by concentration on a rotary evaporator, water (50 mL) was added to the residue, and the suspension was extracted with Et_2O (100 mL x 3). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated. The residue was then purified by flash column chromatography on silica gel (33% EtOAc/hexane) to afford 4-hydroxy-1-(indolin-1-yl)non-8-en-1-one. White solid, 2.38 g, 55% yield.

Starting from 4-hydroxy-1-(indolin-1-yl)non-8-en-1-one (1.85 g, 6.8 mmol), 4-bromo-1-(indolin-1-yl)non-8-en-1-one was synthesized following the bromination procedure in **GP-3**. White solid, 0.75 g, 33% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.04 (t, *J* = 7.4 Hz, 1H), 5.90 – 5.76 (m, 1H), 5.10 – 4.95 (m, 2H), 4.26 – 4.18 (m, 1H), 4.17 – 4.06 (m, 2H), 3.24 (t, *J* = 8.5 Hz, 2H), 2.70 (t, *J* = 7.3 Hz, 2H), 2.46 – 2.32 (m, 1H), 2.23 – 2.07 (m, *J* = 7.0 Hz, 3H), 1.94 (q, *J* = 7.2 Hz, 2H), 1.78 – 1.69 (m, 1H), 1.66 – 1.55 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 142.9, 138.2, 131.1, 127.5, 124.6, 123.7, 116.9, 115.0, 58.4, 47.9, 39.0, 33.84, 33.80, 33.1, 28.0, 26.8.

FT-IR (film) 2932, 1772, 1654, 1599, 1482, 1460, 1412, 1288, 1116, 914, 755 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{23}BrNO$: 336.0958, found: 336.0955.

m.p.: 61 °C.

Radical cyclization experiment (Fig. 4e). In a glovebox, a suspension of $Cu(CH_3CN)_4PF_6$ (4.5 mg, 0.012 mmol, 12 mol%), *rac*-**P** (5.2 mg, 0.0050 mmol, 5.0 mol%), (*S*,*S*)-**N2*** (3.6 mg, 0.015 mmol, 15 mol%), and CsOPh·H_2O (36.6 mg, 0.15 mmol, 1.5 equiv) in anhydrous 2-Me-THF (3.0 mL) in a 4 mL vial was stirred at room temperature for 30 min. Next, 4-CF_3-benzamide (18.9 mg, 0.10 mmol, 1.0 equiv) was weighed into the vial, and then 4-bromo-1-(indolin-1-yl)non-8-en-1-one (40.2 mg, 0.12 mmol, 1.2 equiv) was added. The vial was sealed with a polypropylene screw cap, transferred out of the glovebox, placed into a cryocool with a well-stirred isopropanol bath precooled to −5 °C, and fixed upside down with a copper wire holder. The reaction mixture was stirred at −5 °C for 5 min, and then it was irradiated with two PR 440 nm Kessil blue LED lamps, placed ~5 cm away, for 24. The resulting solution was then concentrated, and the residue was purified by preparative TLC. The yield and the diastereoselectivity were determined by ^{19}F NMR.

^{1}H NMR (400 MHz, $CDCl_3$) diastereomeric mixture, δ 8.21 – 7.84 (m, 4H), 7.73 and 7.57 (d, *J* = 8.2 Hz, 2H), 7.14 – 7.07 (m, 2H), 6.00 – 6.95 (m, 1H), 4.21 – 3.90 (m, 3H), 3.14 (t, *J* = 8.4 Hz, 2H), 3.04 – 2.97 (m, 1H), 2.53 – 2.32 (m, 2H), 2.14 – 1.37 (m, 8H), 1.28 – 1.02 (m, 2H).

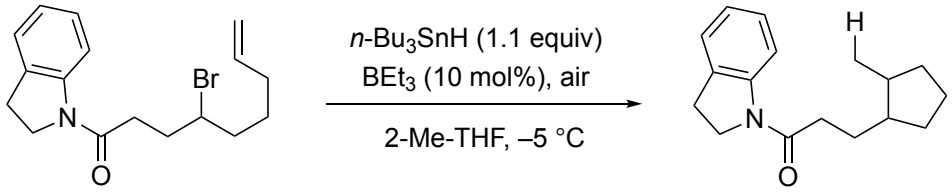
^{13}C NMR (101 MHz, $CDCl_3$) diastereomeric mixture, δ 171.6 and 171.4, 166.4, 142.8 and 142.7, 138.5 and 138.2, 132.7 (q, *J* = 32.4 Hz) and 132.6 (q, *J* = 32.4 Hz), 131.2 and 131.1, 128.3 and 128.0, 127.3, 126.1 (q, *J* = 272.0 Hz), 125.3 (q, *J* = 3.8 Hz) and 125.2 (q, *J* = 3.8 Hz), 124.8, 124.1 and 124.0, 116.9, 47.9 and 47.8, 45.0 and 44.0, 43.7 and 40.4, 42.7 and 40.1, 34.1 and 33.5, 32.9 and 30.3, 30.4 and 28.0, 29.5 and 27.4, 24.0 and 21.9, 21.3.

FT-IR (film) 2948, 2863, 2360, 2341, 1665, 1481, 1407, 1286, 752 cm^{-1}.

^{19}F NMR (282 MHz, $CDCl_3$) diastereomeric mixture, δ –62.75, –62.83.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{25}H_{28}F_3N_2O_2$: 445.2097, found: 445.2095.

m.p.: 106-109 °C.



Cyclization of 4-bromo-1-(indolin-1-yl)non-8-en-1-one in the presence of *n*-Bu_3SnH. Following a literature procedure,[17] the cyclization of 4-bromo-1-(indolin-1-yl)non-8-en-1-one was conducted on a 0.10 mmol scale in 2-Me-THF. 80% yield, 3:1 d.r.

^{1}H NMR (400 MHz, $CDCl_3$) diastereomeric mixture, δ 8.17 (d, *J* = 8.0 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.95 – 6.91 (m, 1H), 3.98 (t, *J* = 8.5 Hz, 2H), 3.12 (t, *J* = 8.4 Hz, 2H), 2.43 – 2.26 (m, 2H), 2.00 – 1.91 (m, 1H), 1.85 – 1.05 (m, 9H), 0.93 and 0.77 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) diastereomeric mixture, δ 171.70 and 171.66, 143.2 and 139.1, 131.0, 127.6, 124.5, 123.4, 117.0 and 114.3, 48.0 and 47.3, 42.9 and 40.7, 36.1 and 35.2, 35.3 and 34.8, 33.5 and 32.2, 29.6 and 29.4, 28.1, 25.5 and 23.4, 22.5 and 19.4, 14.9.

FT-IR (film) 2949, 2866, 2361, 2342, 1662, 1482, 1410, 1284, 754 cm^{-1}.

HRMS (LC-MS) *m*/*z* $(M+H)^+$ calcd for $C_{17}H_{24}NO$: 258.1852, found: 258.1848.

m.p.: 43-44 °C.

(*S*)- and (*R*)-Dibenzyl (3-bromobutyl)phosphonate. (*S*) and (*R*)-Dibenzyl (3-bromobutyl)phosphonate were synthesized according to **GP-1** from the corresponding enantioenriched 2-methyloxirane. The characterization data are in accordance with (*rac*)-dibenzyl (3-bromobutyl)phosphonate.

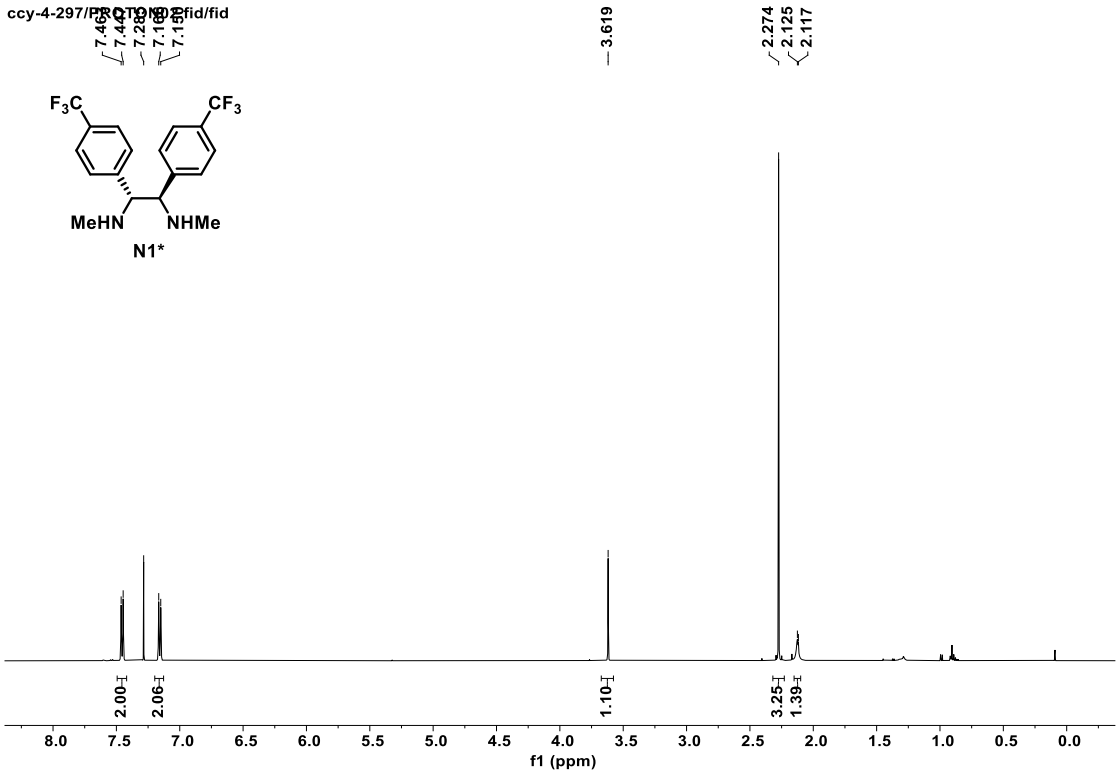
(*S*)-Dibenzyl (3-bromobutyl)phosphonate, >99% ee; (*R*)-dibenzyl (3-bromobutyl) phosphonate, >99% ee.

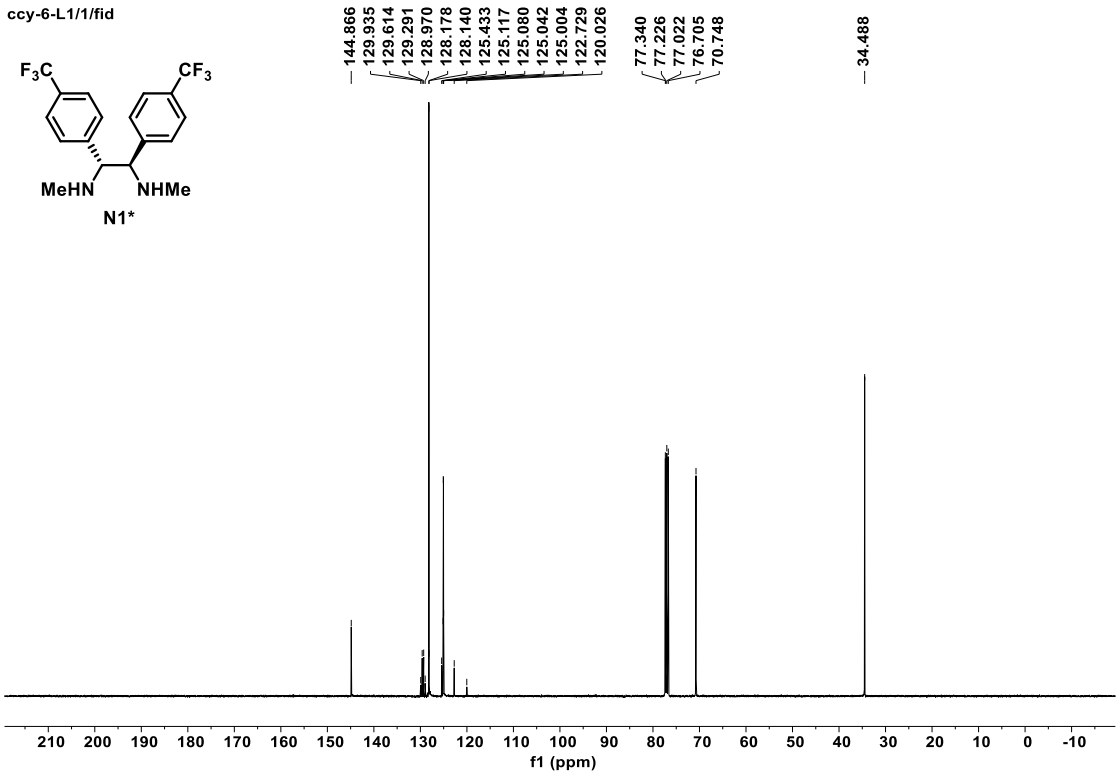
The ee was determined via SFC on a CHIRALPAK AD-3 column (15% *i*-PrOH in supercritical CO_2, 2.5 mL/min); retention times for (*S*): 9.8 min, (*R*): 9.1 min.

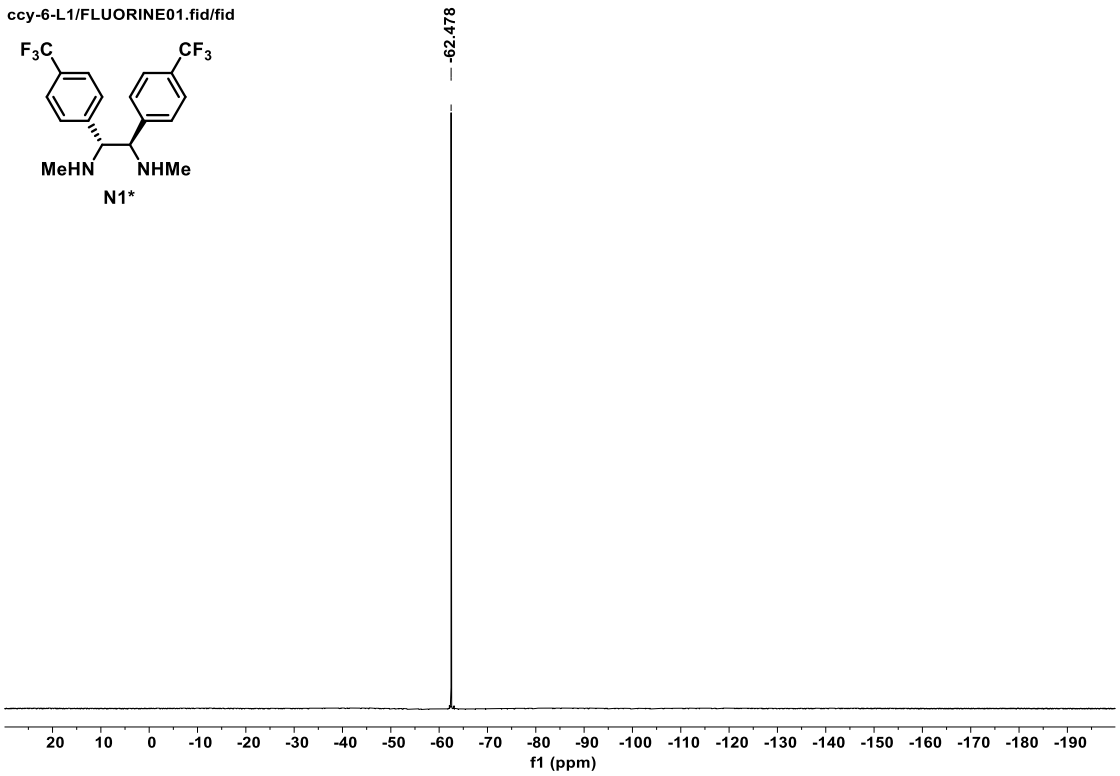
$[\alpha]^{24}_D$ = –23 (*c* 1.6, $CHCl_3$); for (*R*)-dibenzyl (3-bromobutyl) phosphonate, >99% ee.

Couplings with enantioenriched γ-bromophosphonate (Fig. 4f). GP-10 was followed, under the indicated reaction conditions.

XI. NMR Spectra and Stereoselectivity Analysis



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CF3
MeHN
NHMe
N1*
-62.478
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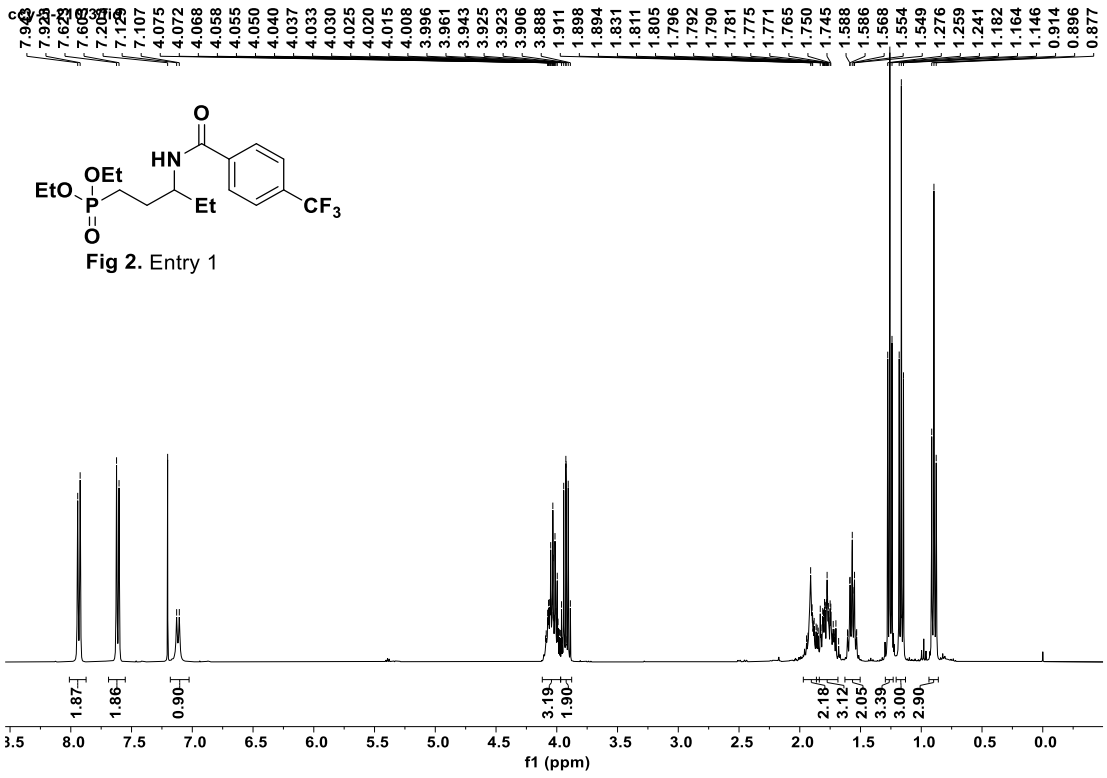
f1 (ppm)



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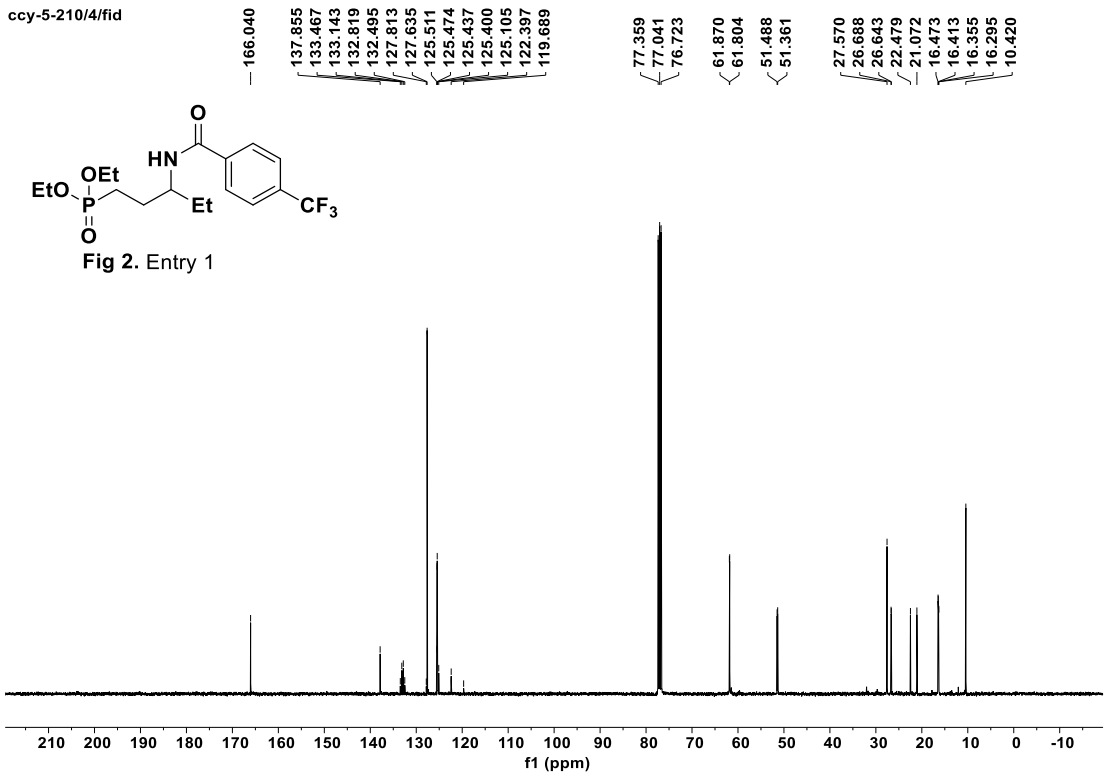


Fig 2. Entry 1

ccy-5-210/5/fid

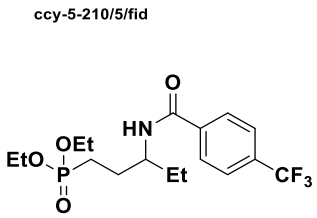


Fig 2. Entry 1

ccy-5-210/FLUORINE01.fid/fid

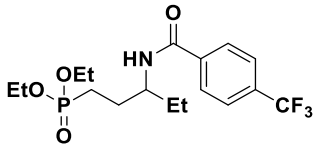


Fig 2. Entry 1

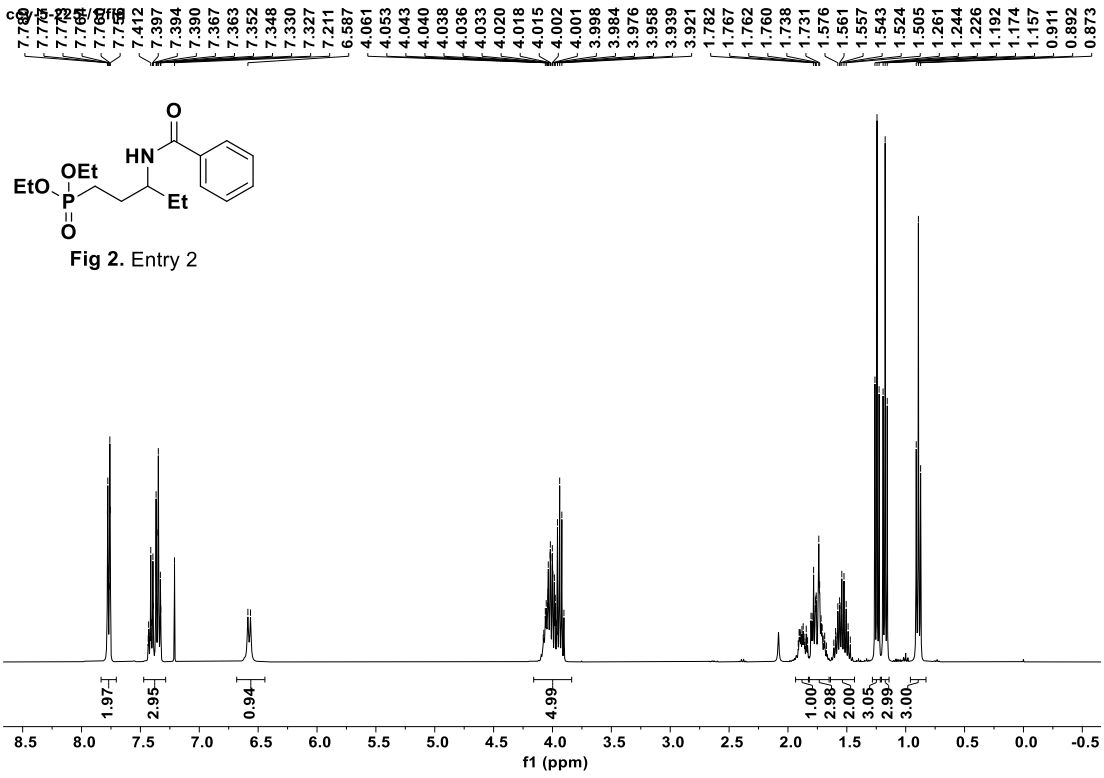


Fig 2. Entry 2

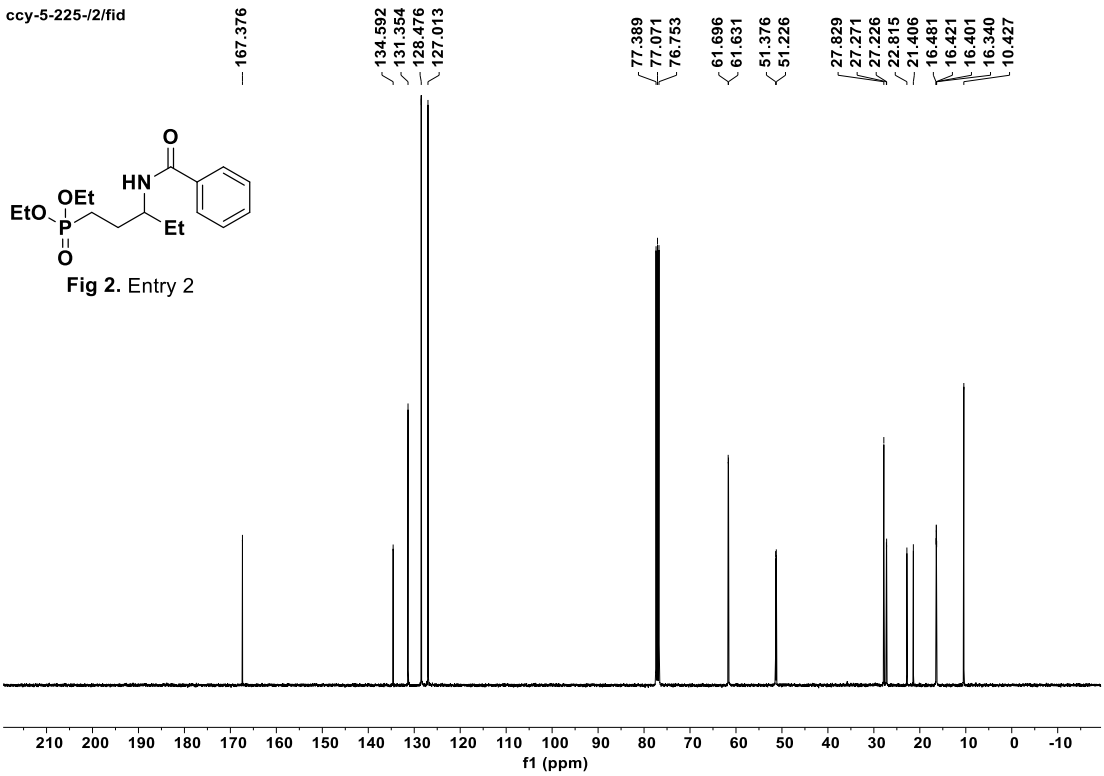
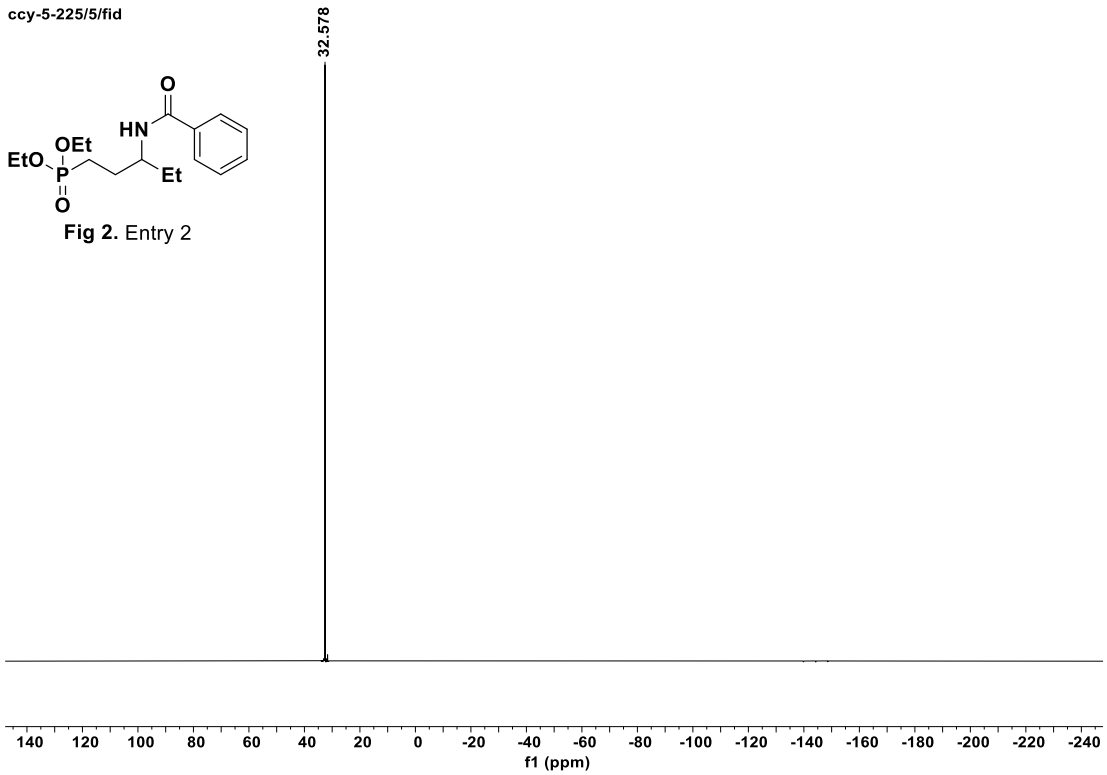


Fig 2. Entry 2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EtO
OEt
P
O
Et
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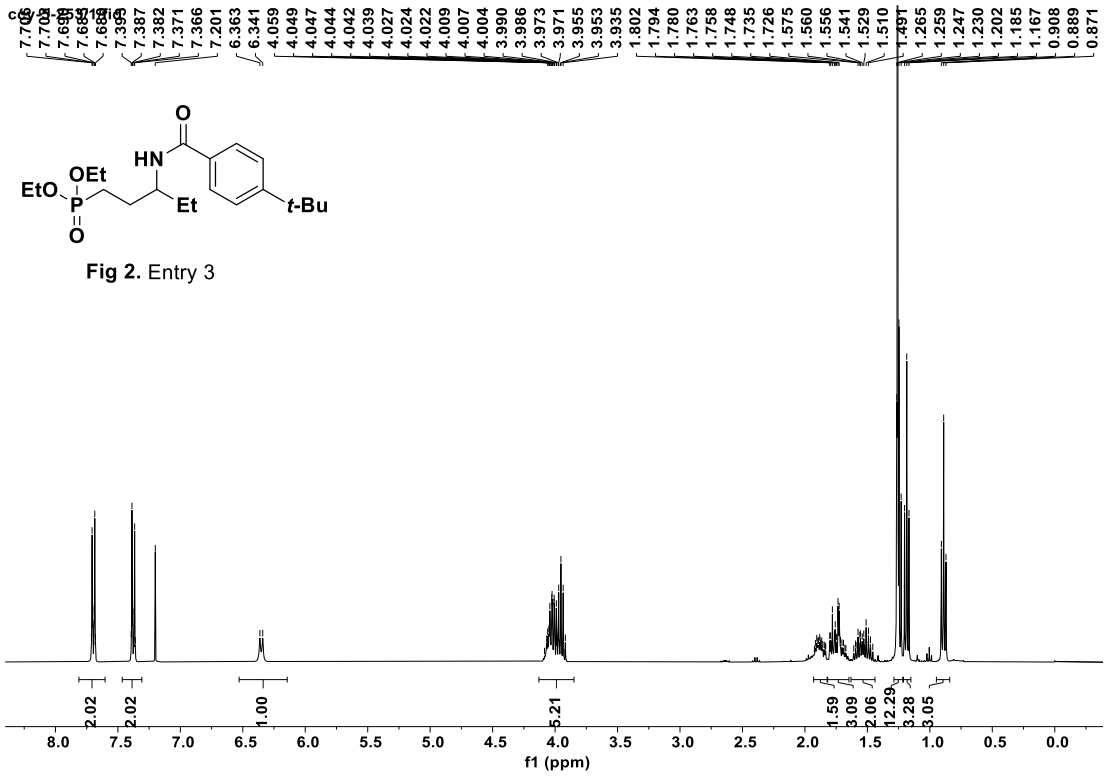
f1 (ppm)

Fig 2. Entry 2



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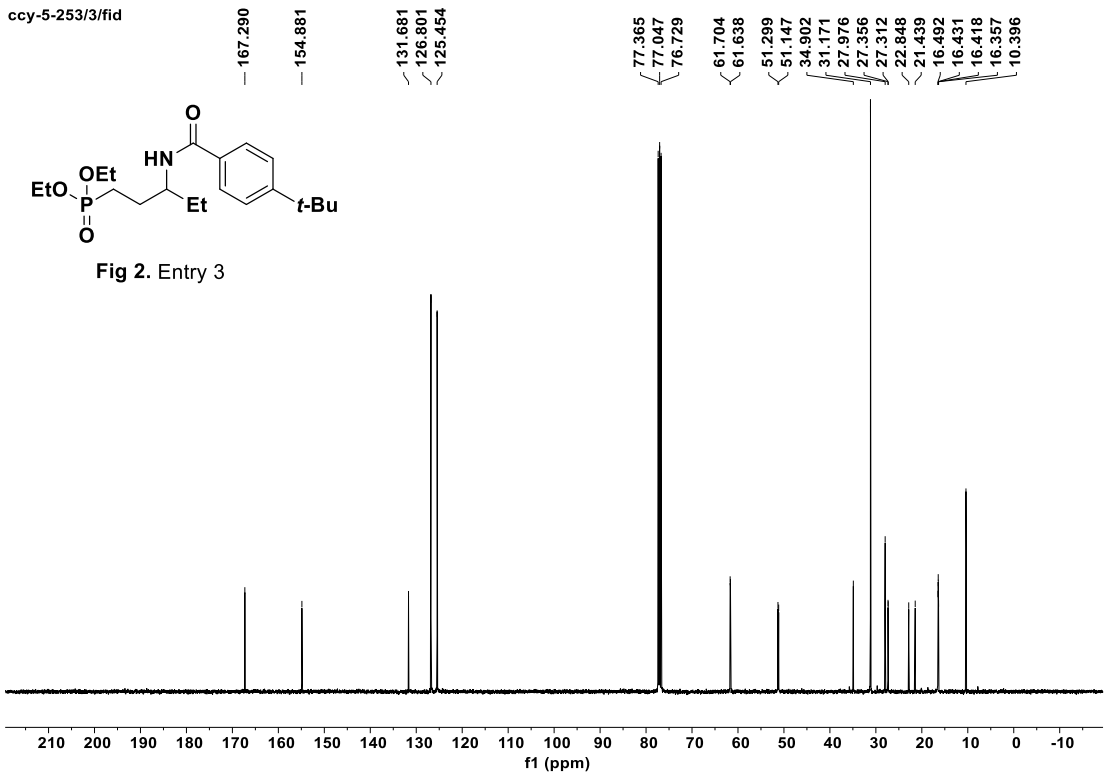
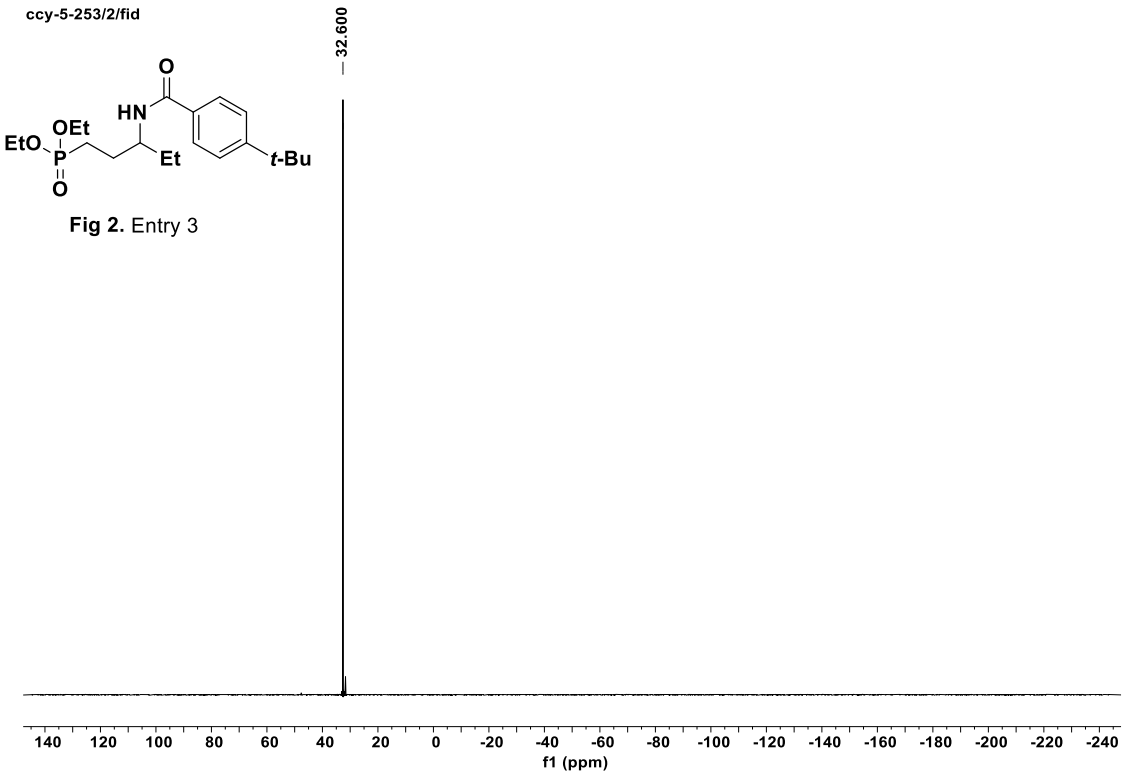


Fig 2. Entry 3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EtO
OEt
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Et
t-Bu
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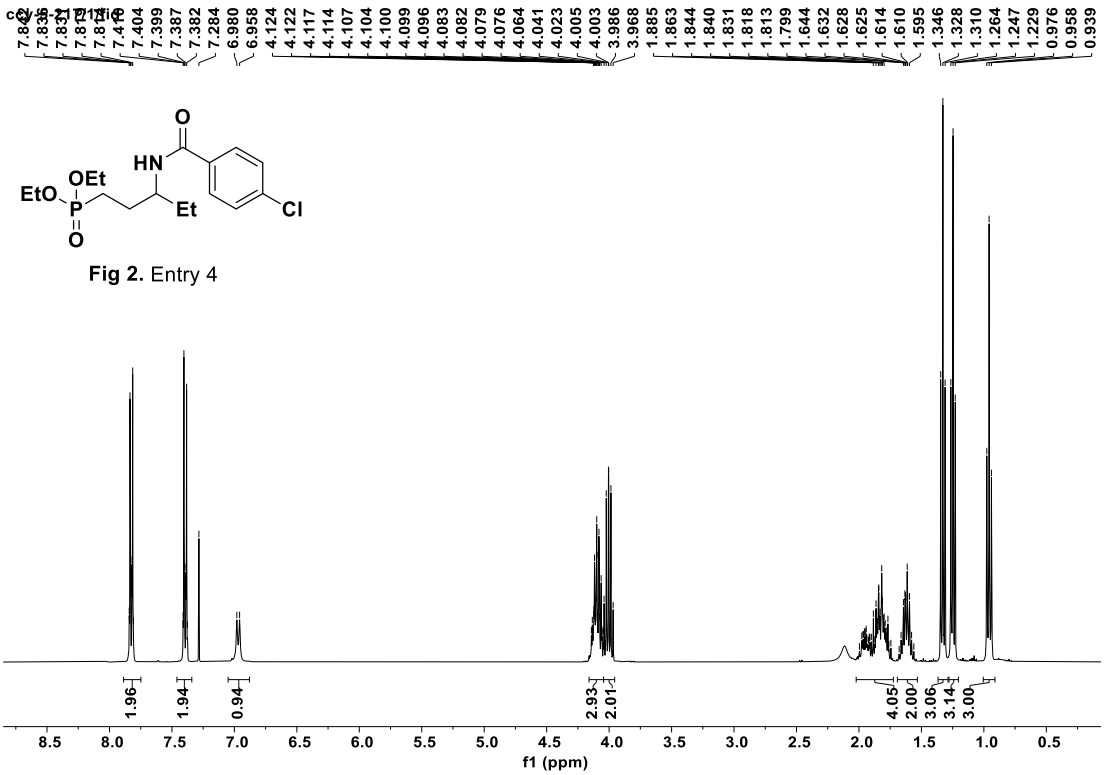
f1 (ppm)

Fig 2. Entry 3



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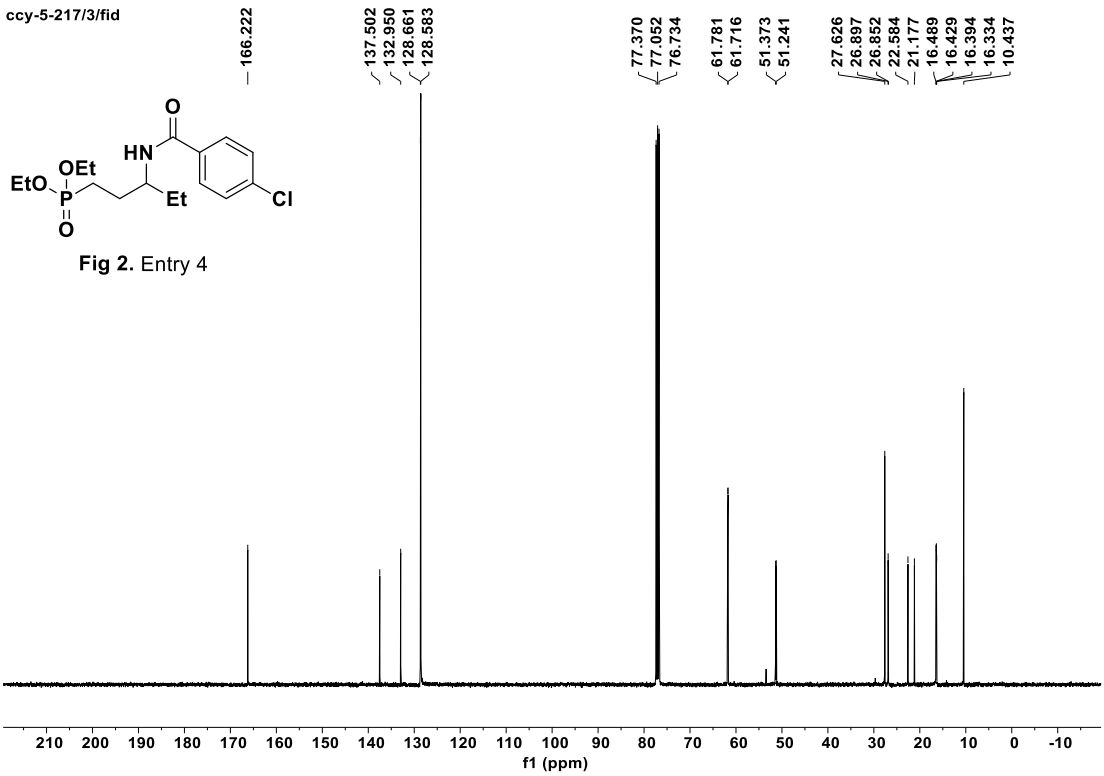

Fig 2. Entry 4


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EtO
OEt
P
O
Et
Cl
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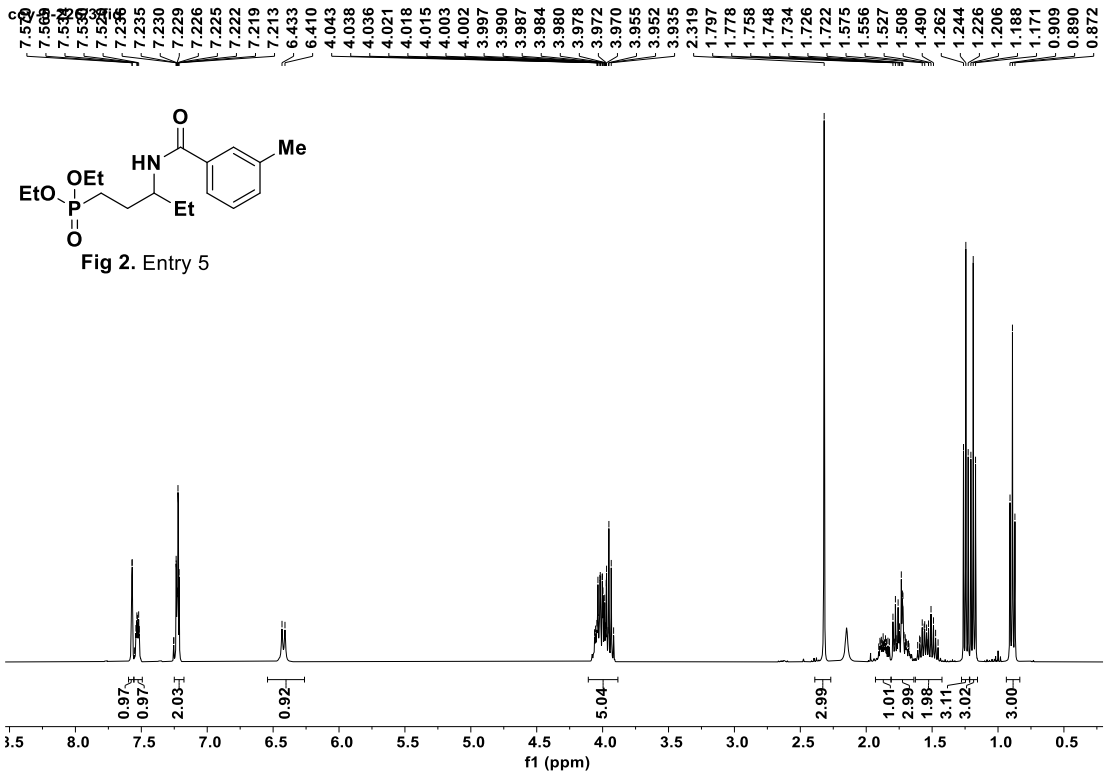
f1 (ppm)

Fig 2. Entry 4



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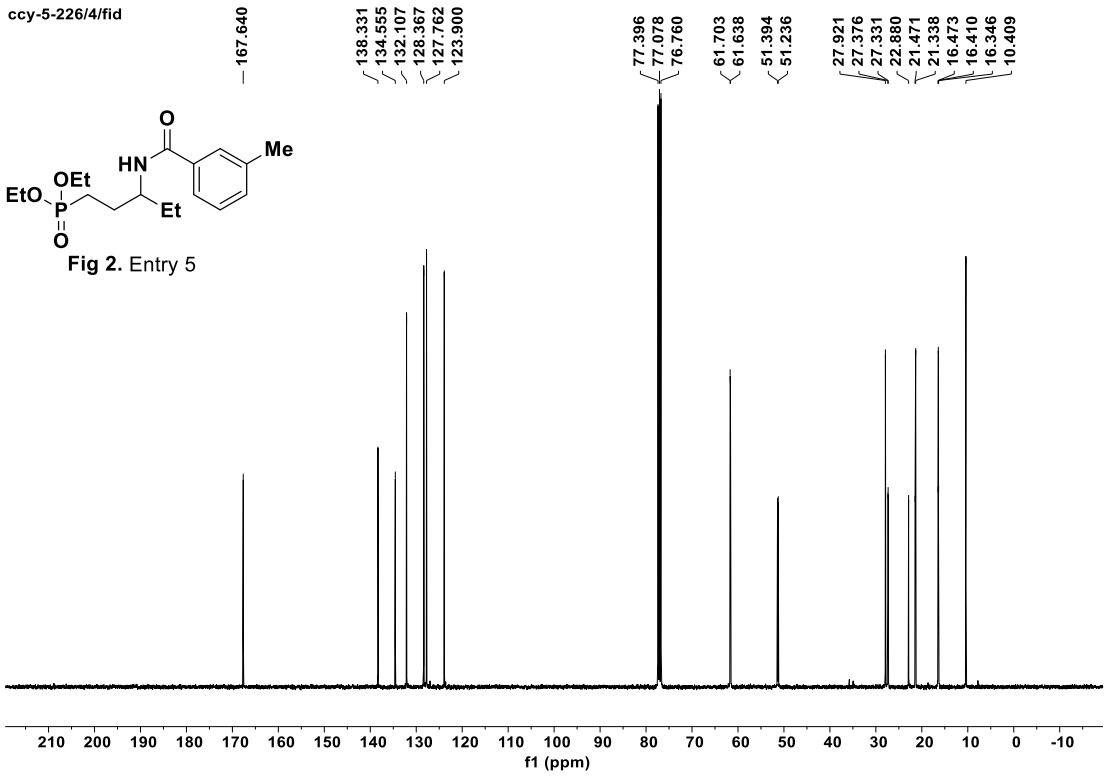
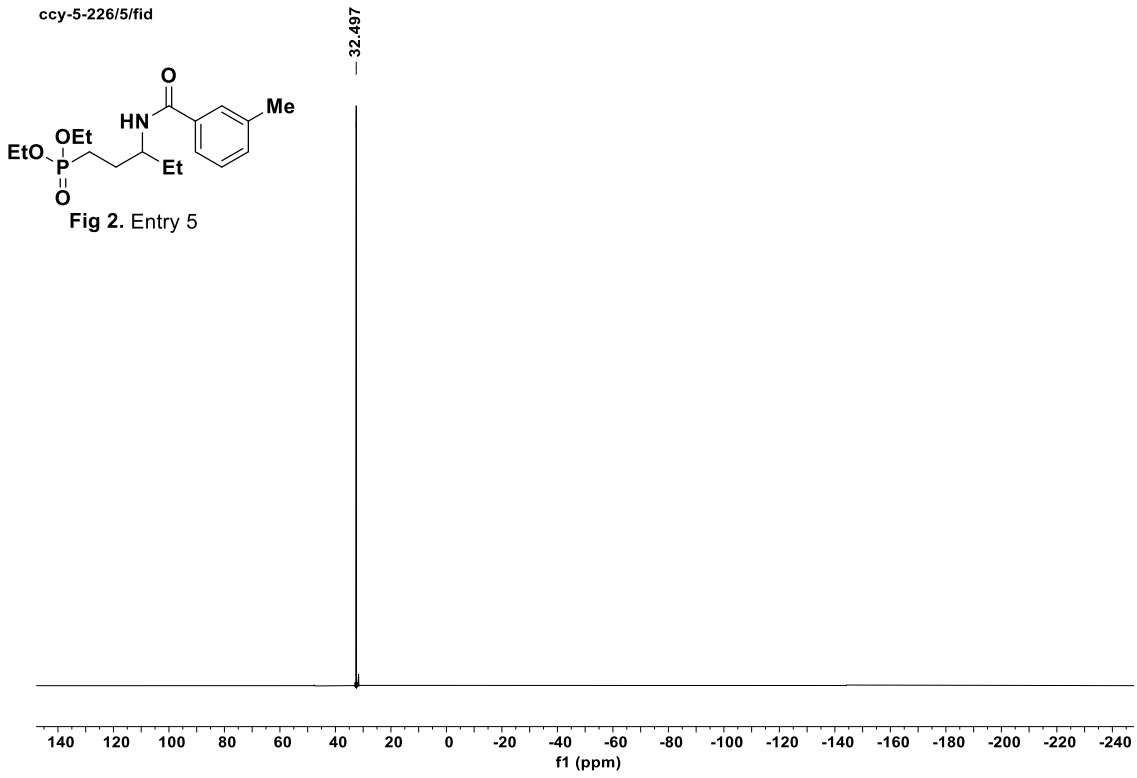


Fig 2. Entry 5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EtO
P
Et
O
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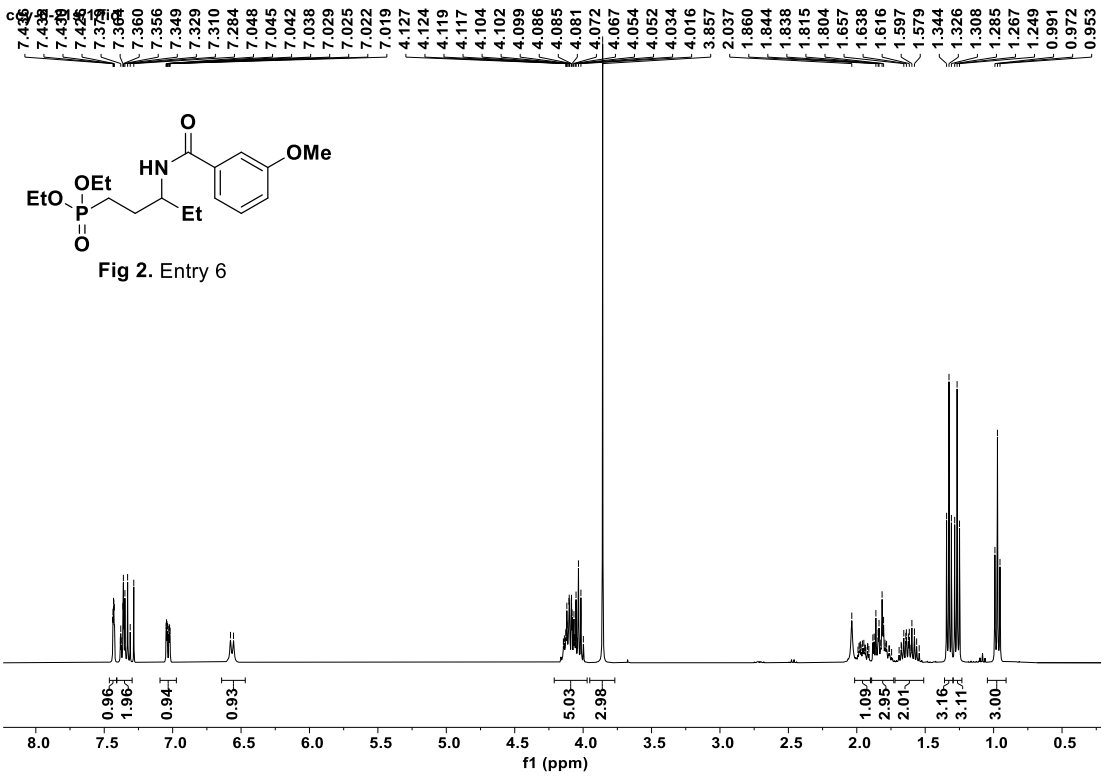
f1 (ppm)

Fig 2. Entry 5



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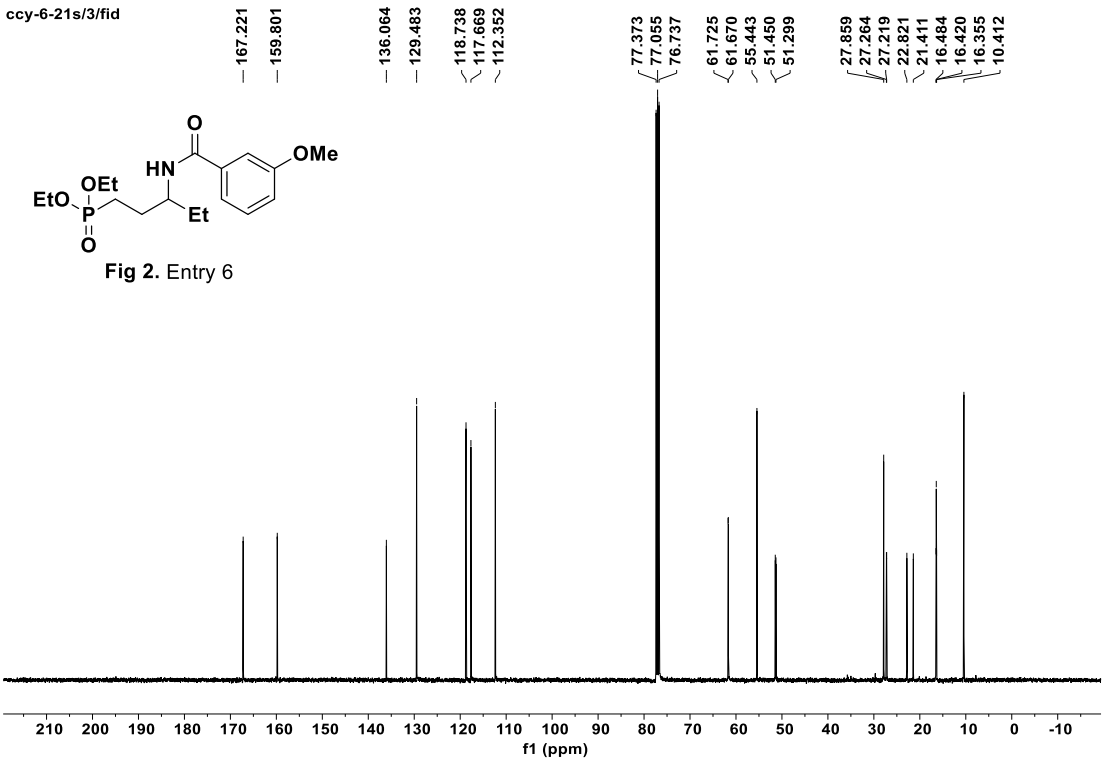

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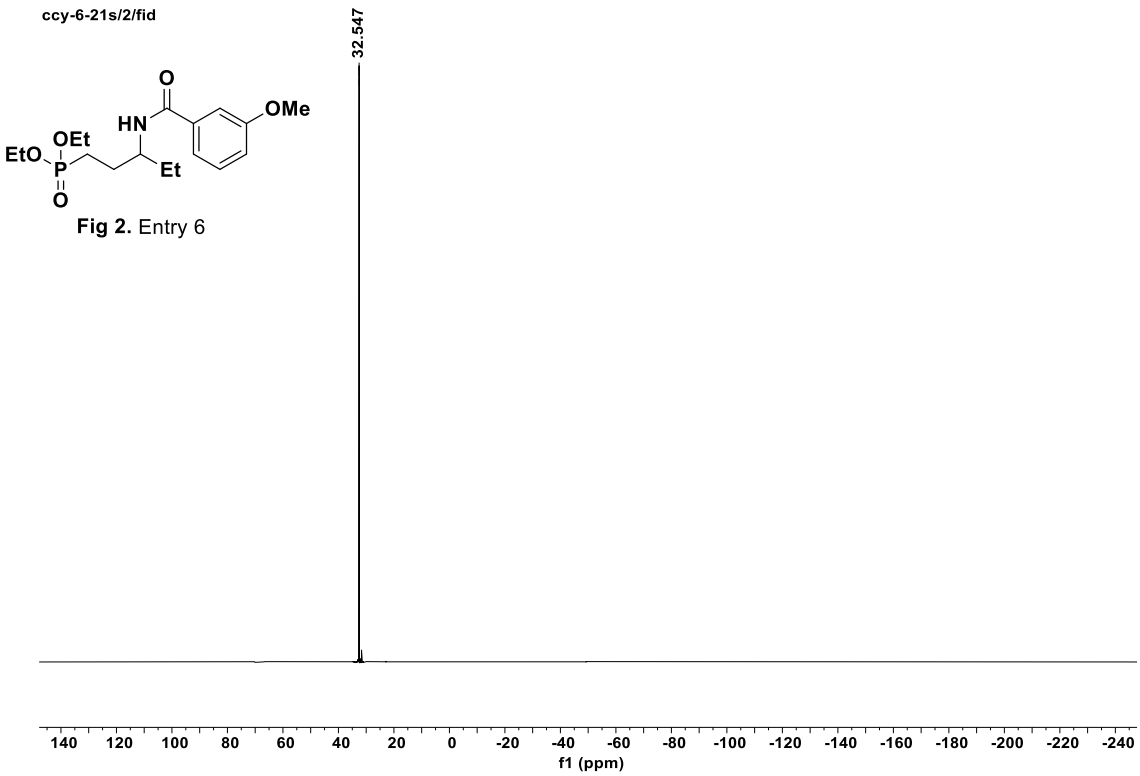
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OMe
EtO
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Et
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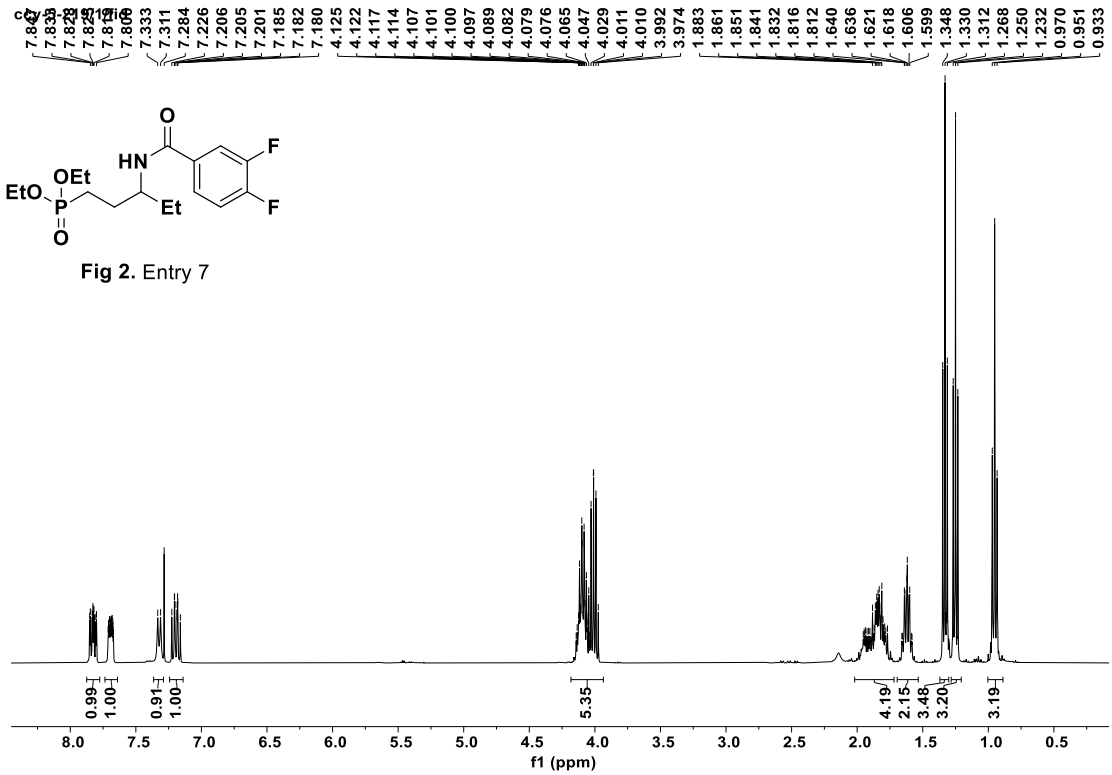
f1 (ppm)

Fig 2. Entry 6



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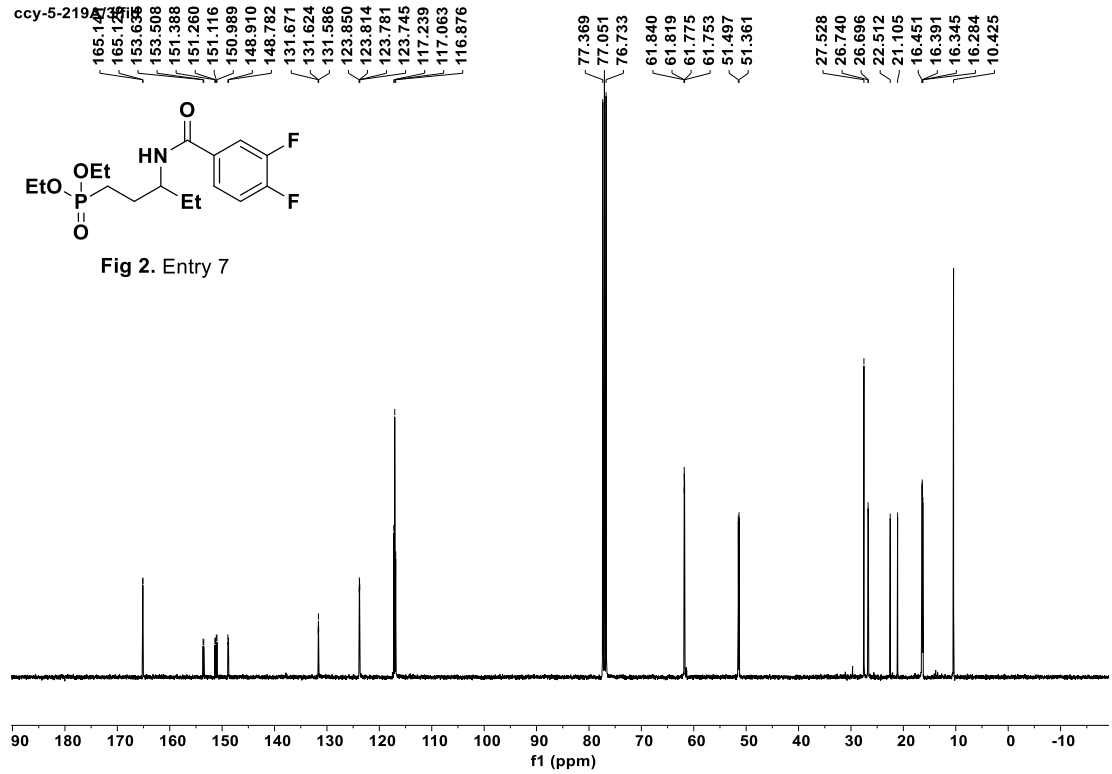

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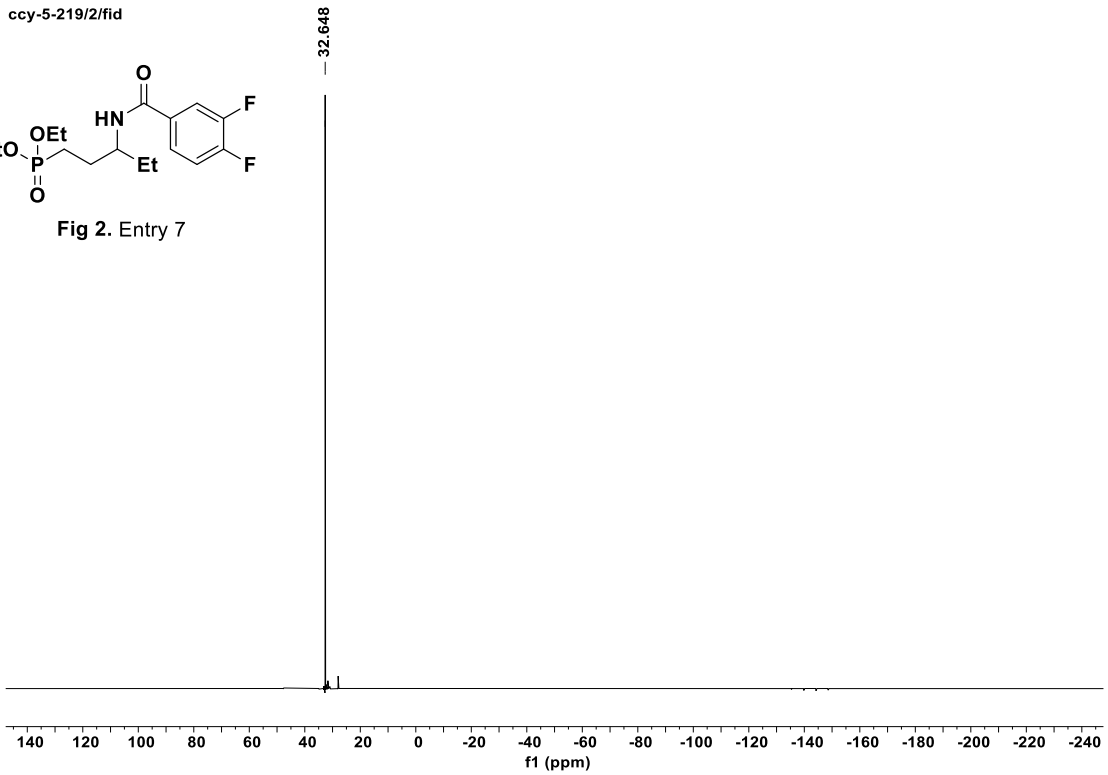

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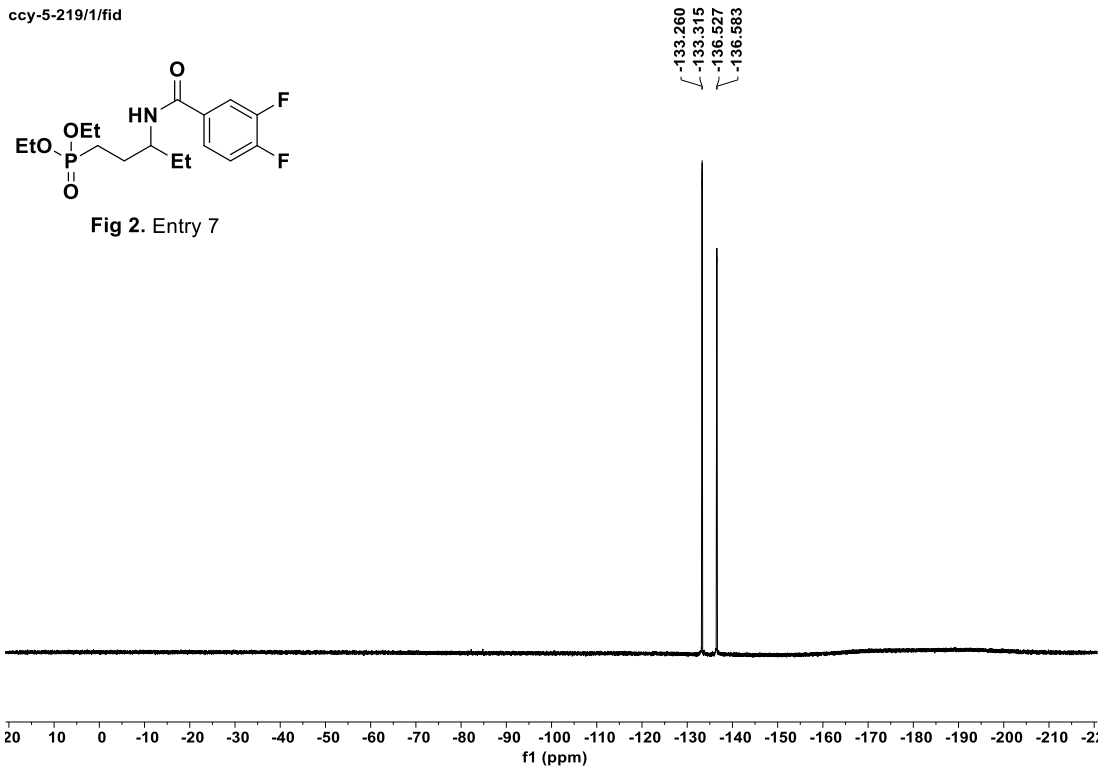

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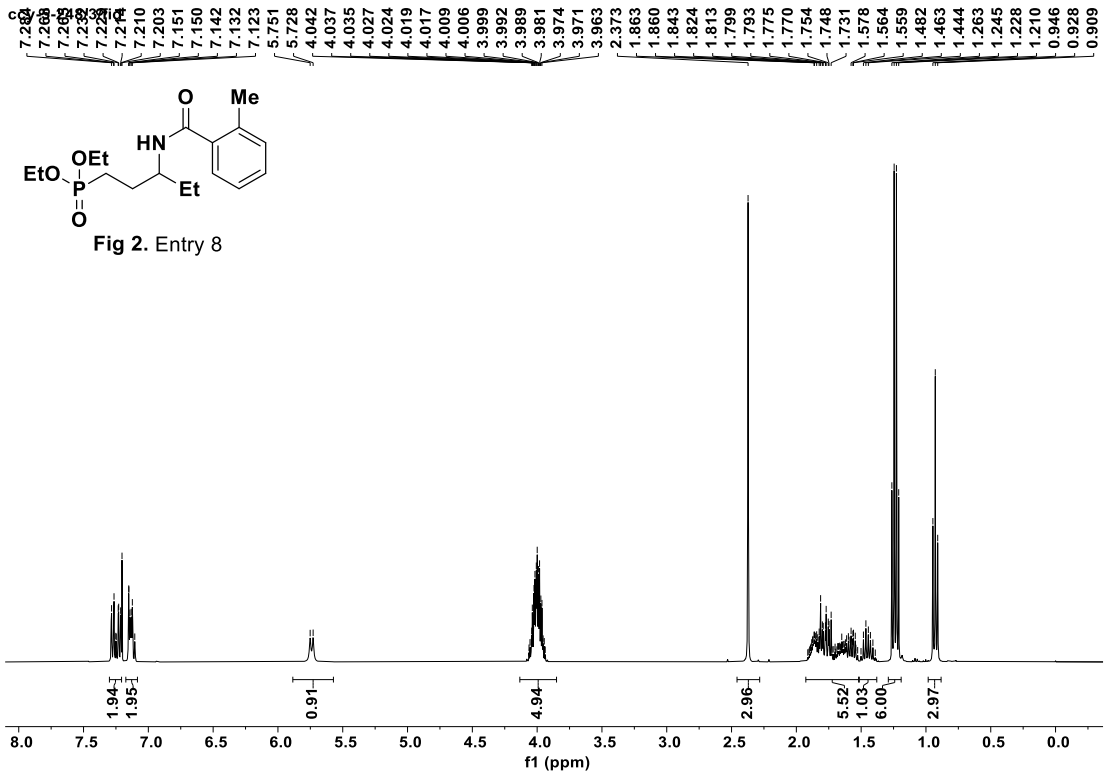
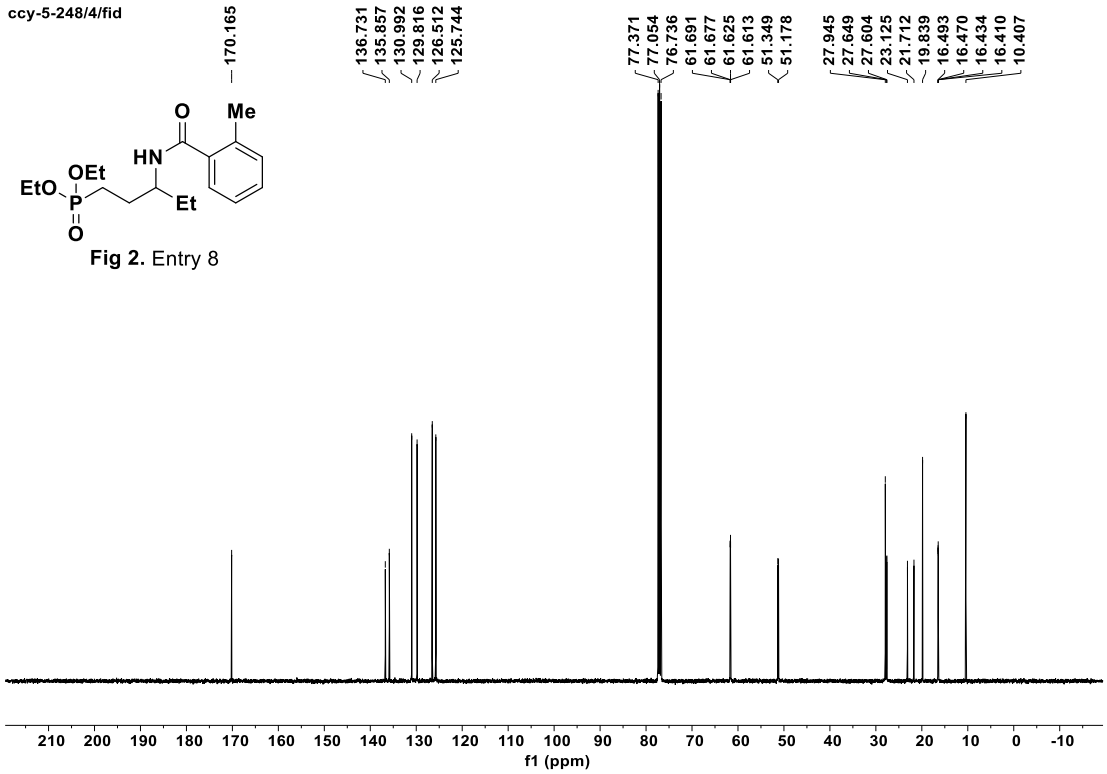


Fig 2. Entry 8



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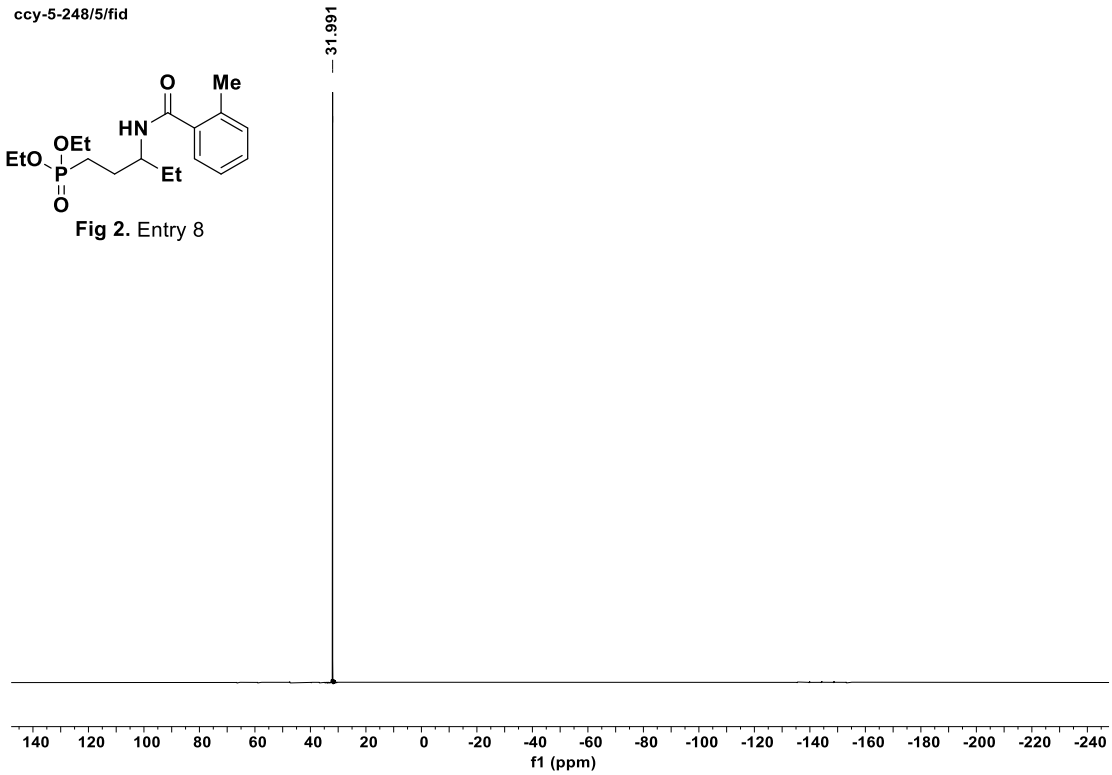
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P
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-220
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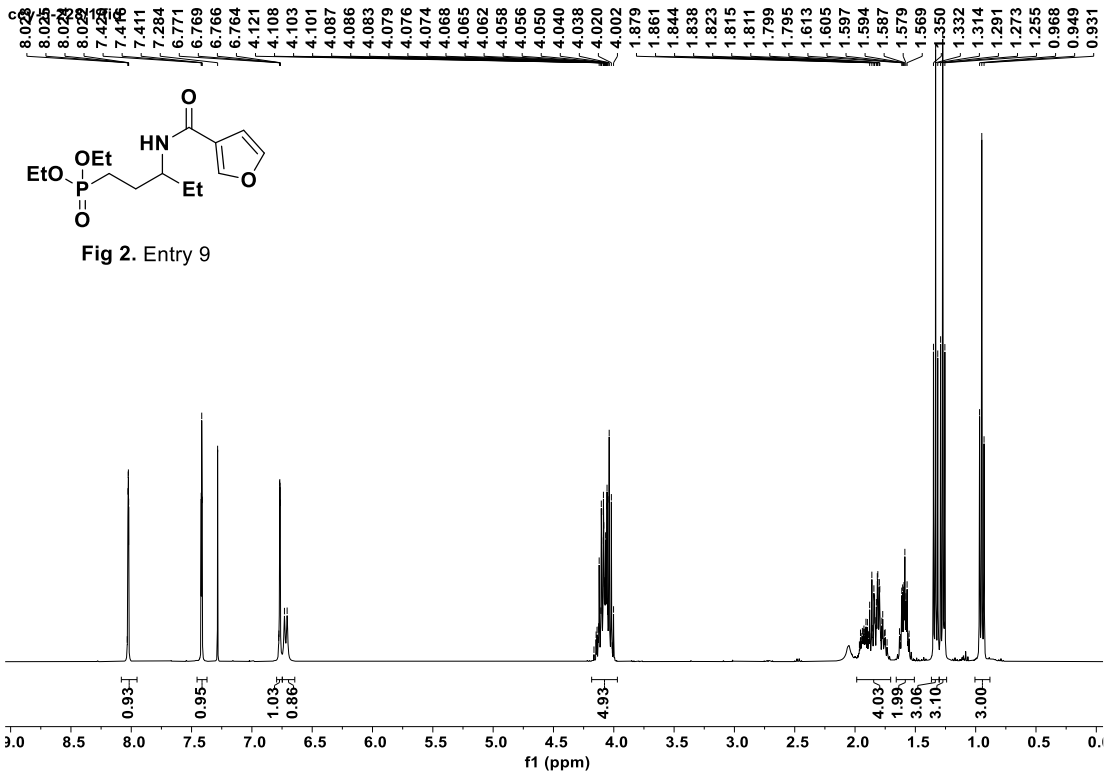
f1 (ppm)

Fig 2. Entry 8



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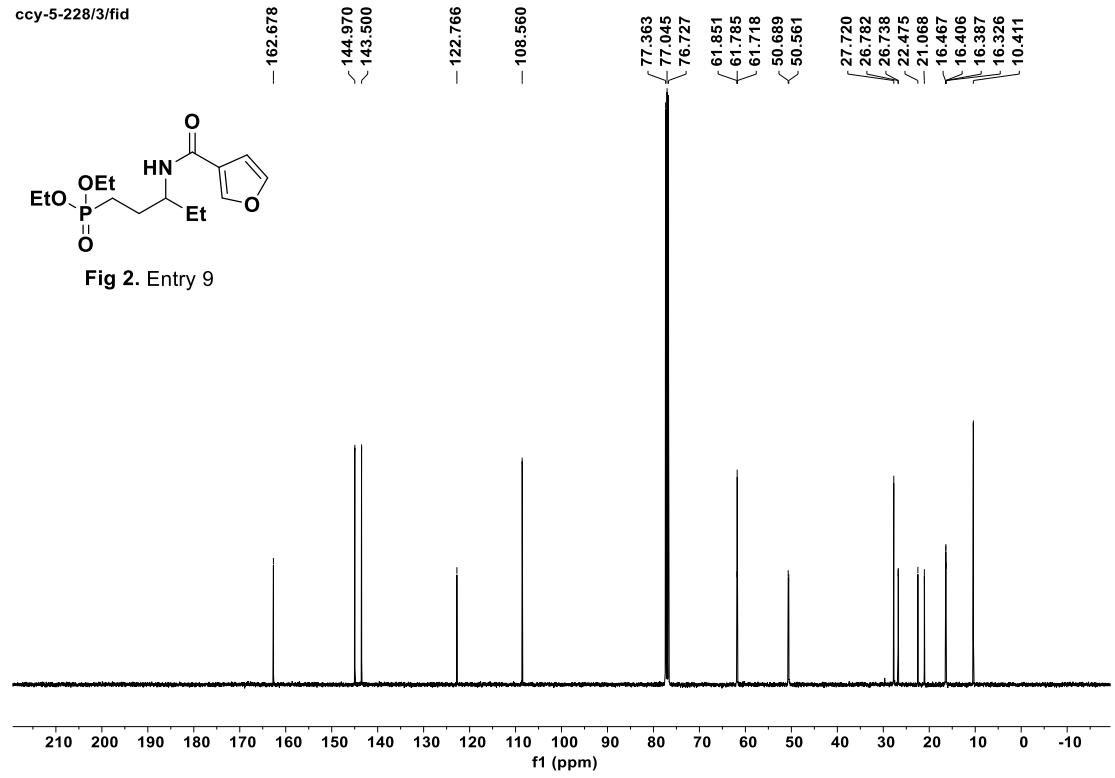

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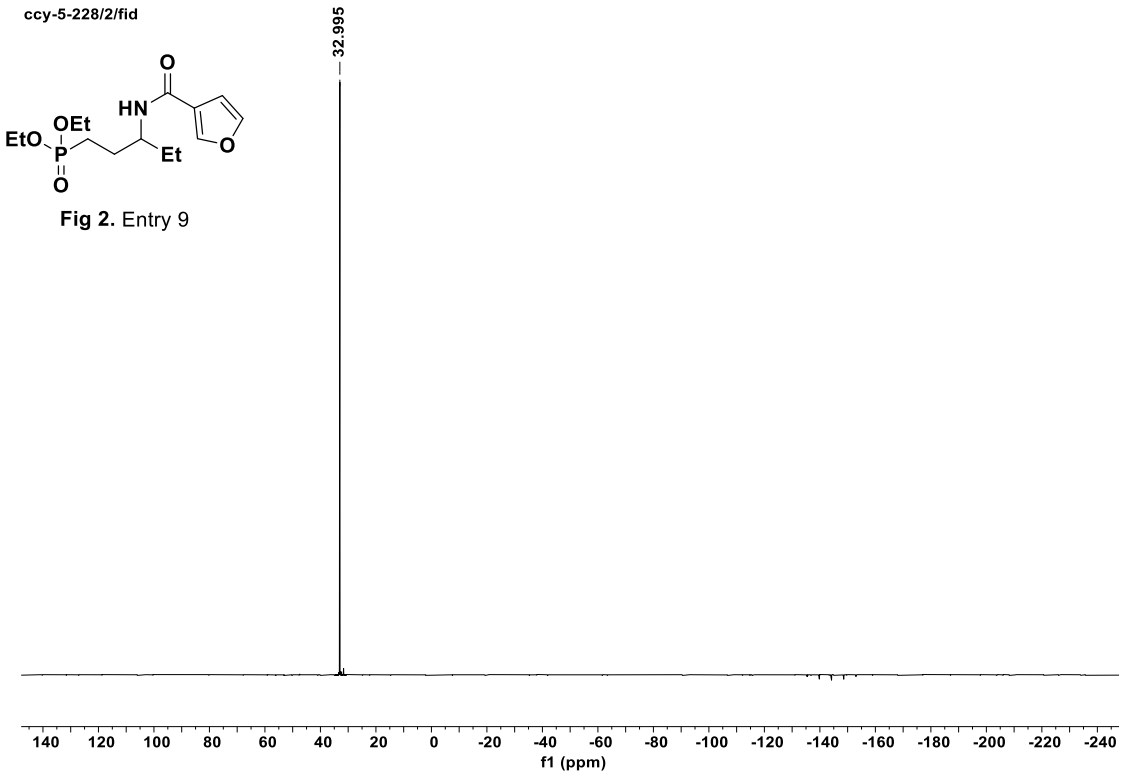
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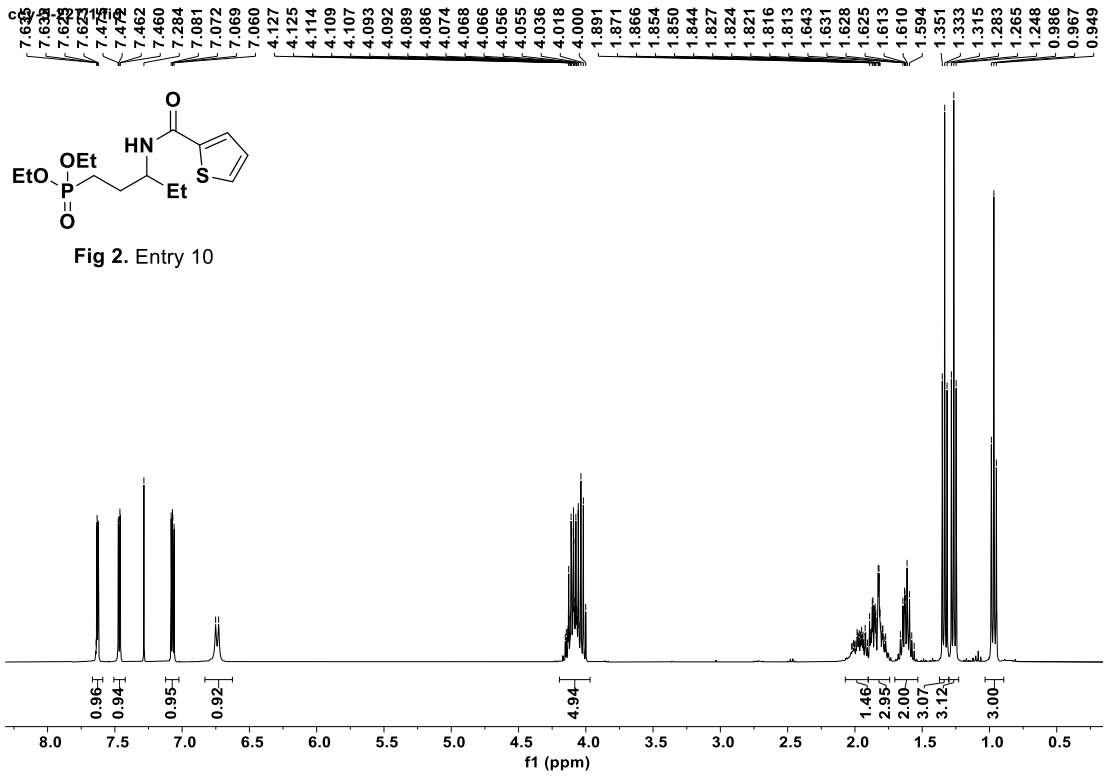
f1 (ppm)

Fig 2. Entry 9



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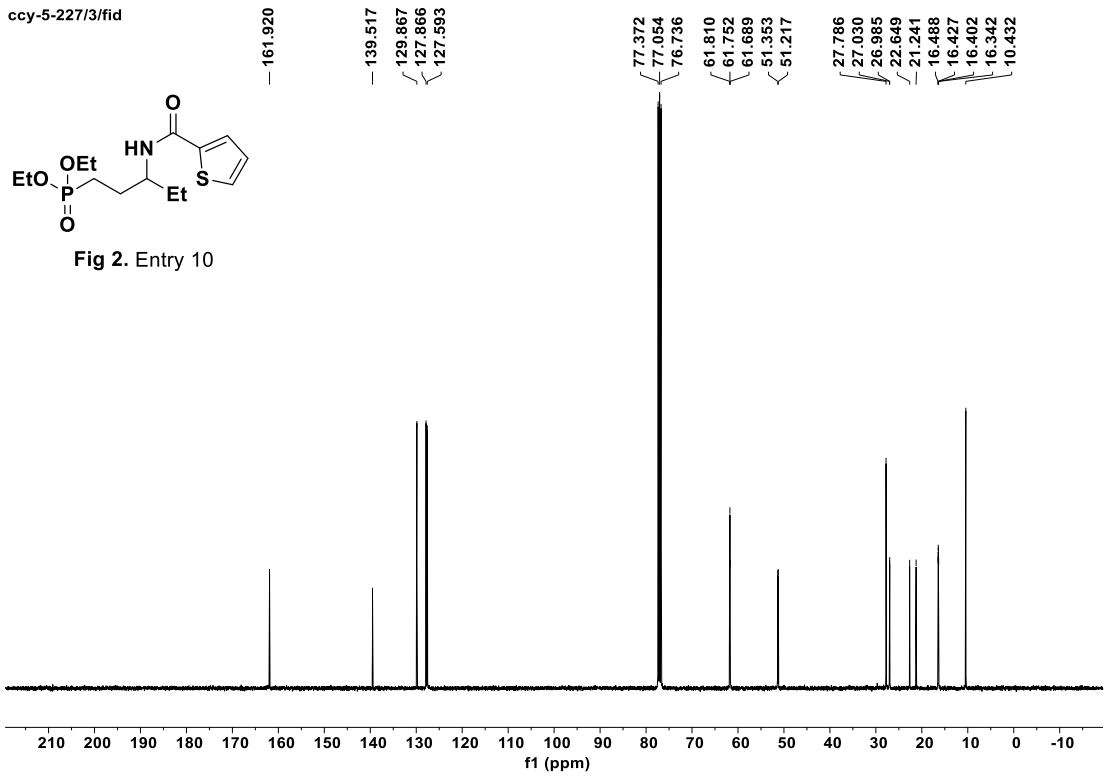


Fig 2. Entry 10

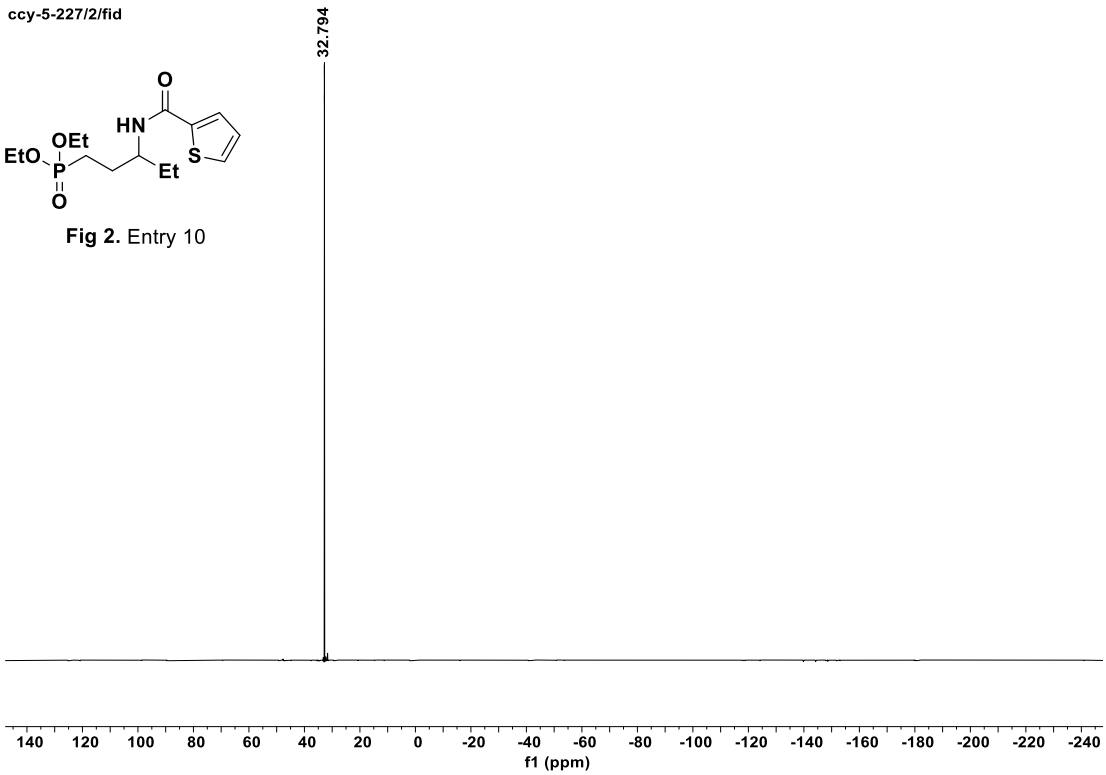


Fig 2. Entry 10

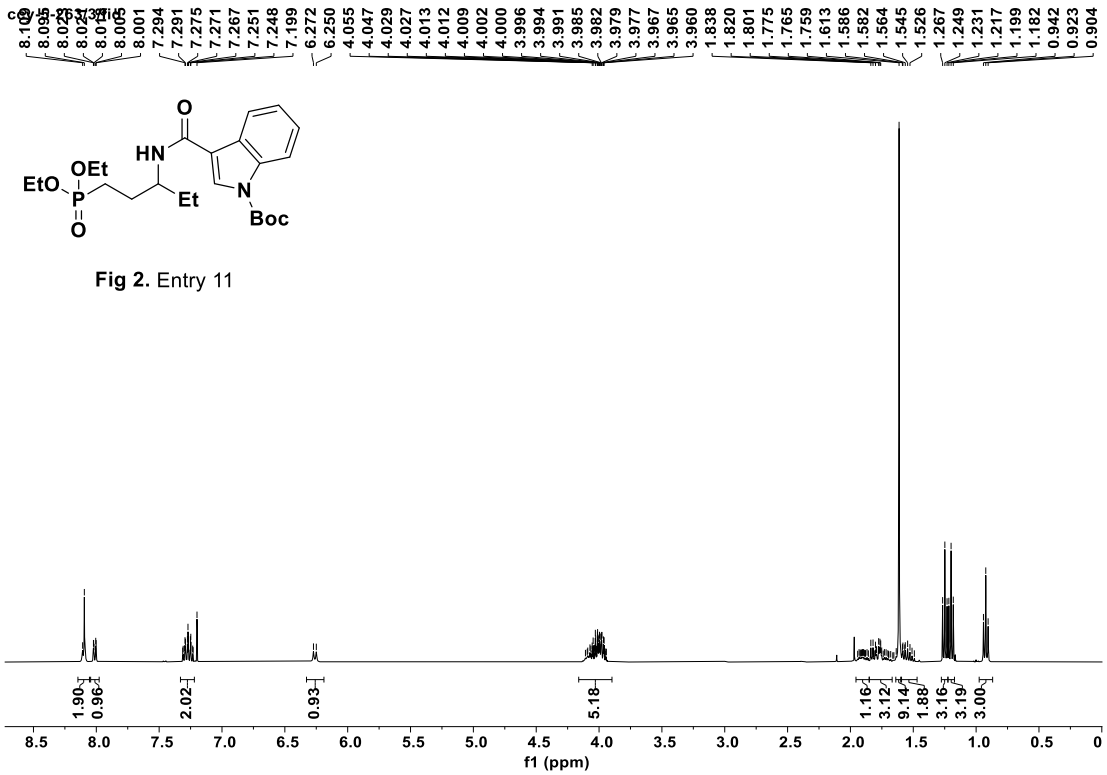


Fig 2. Entry 11

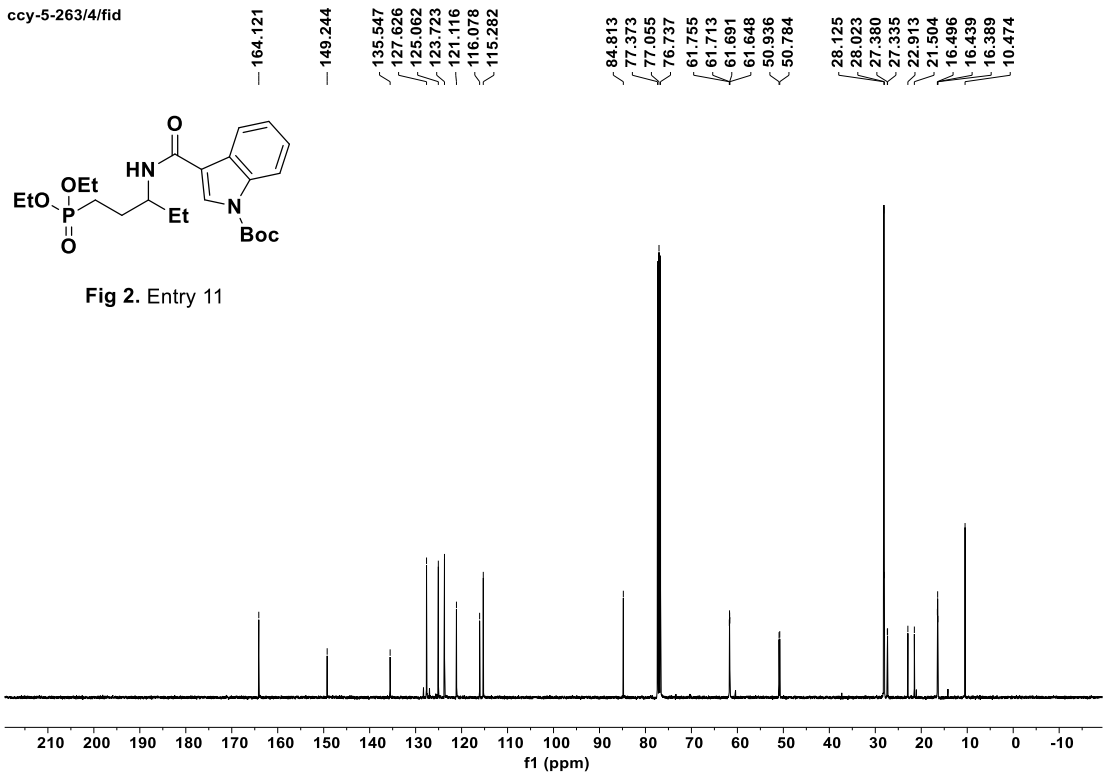


Fig 2. Entry 11

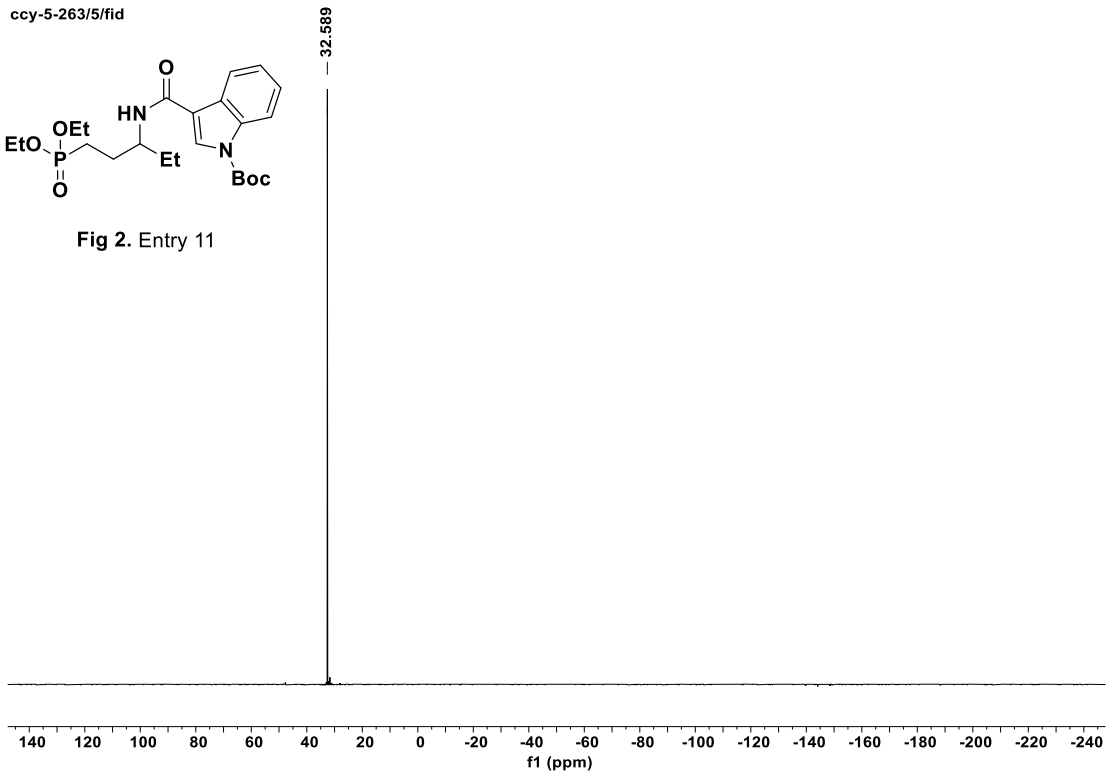


Fig 2. Entry 11

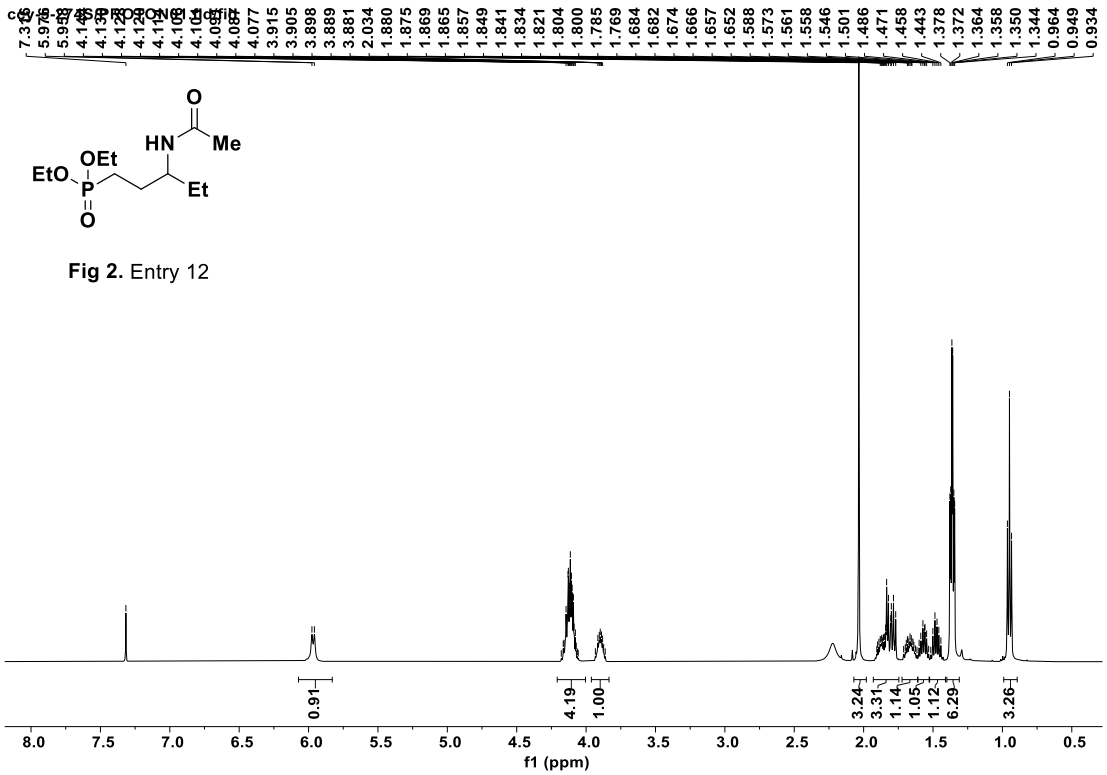


Fig 2. Entry 12

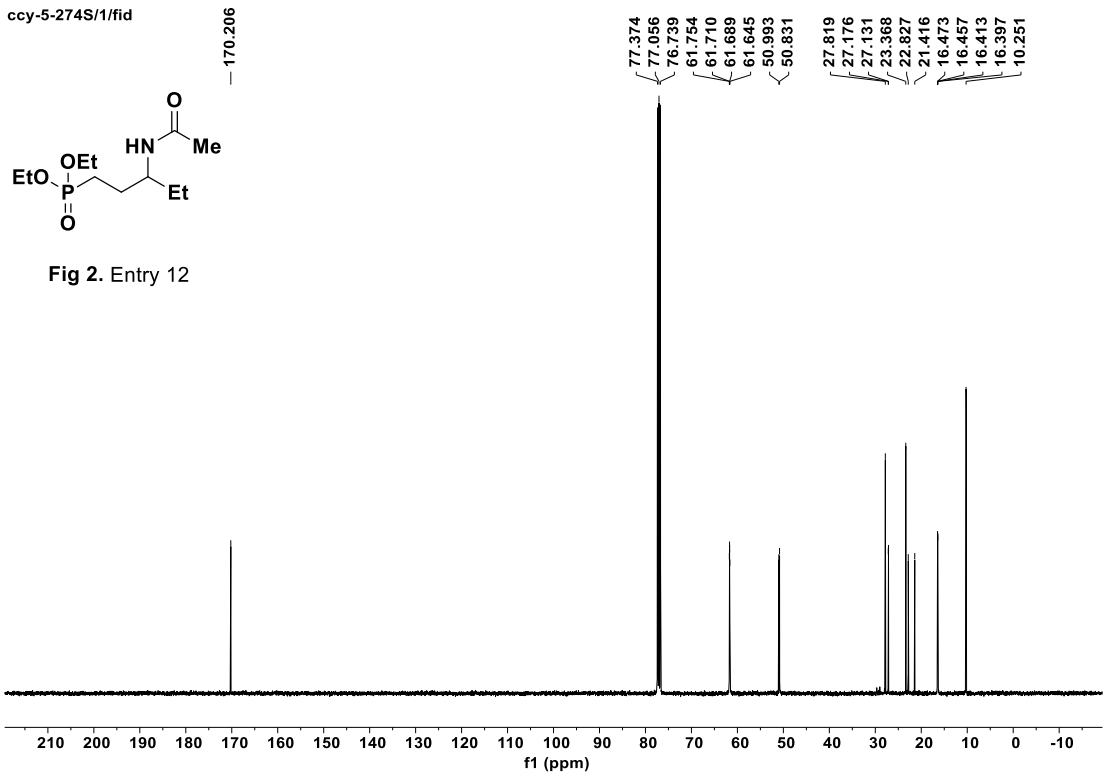


Fig 2. Entry 12

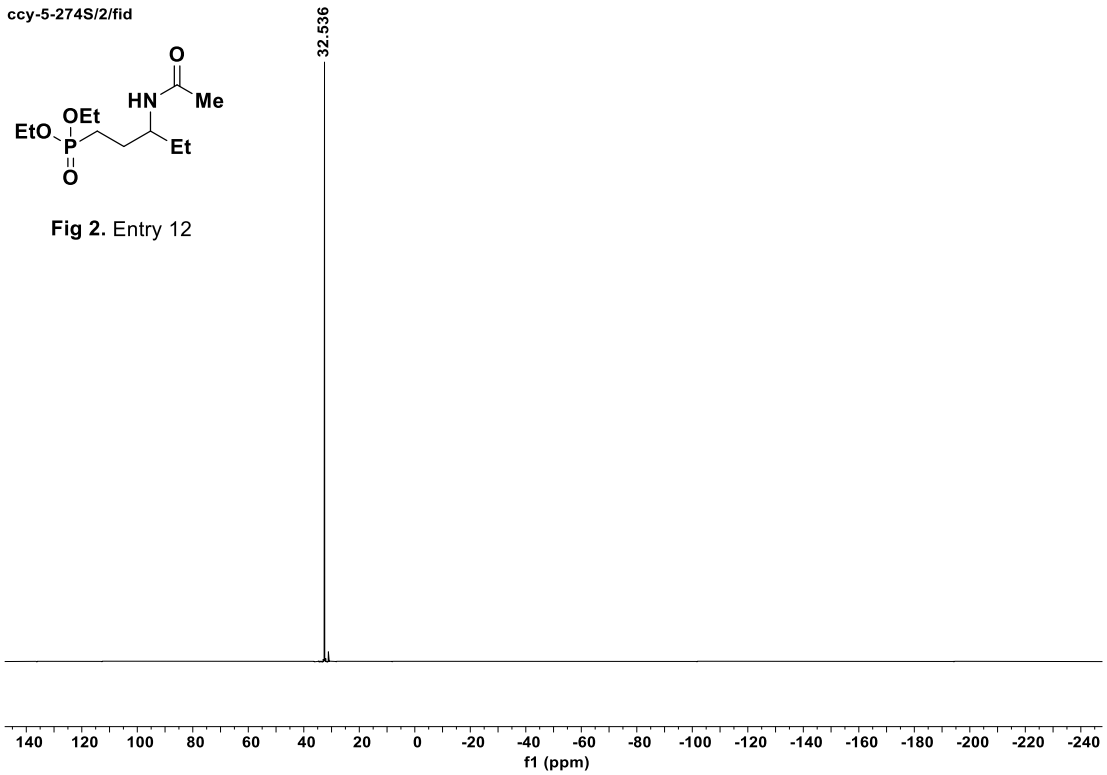


Fig 2. Entry 12

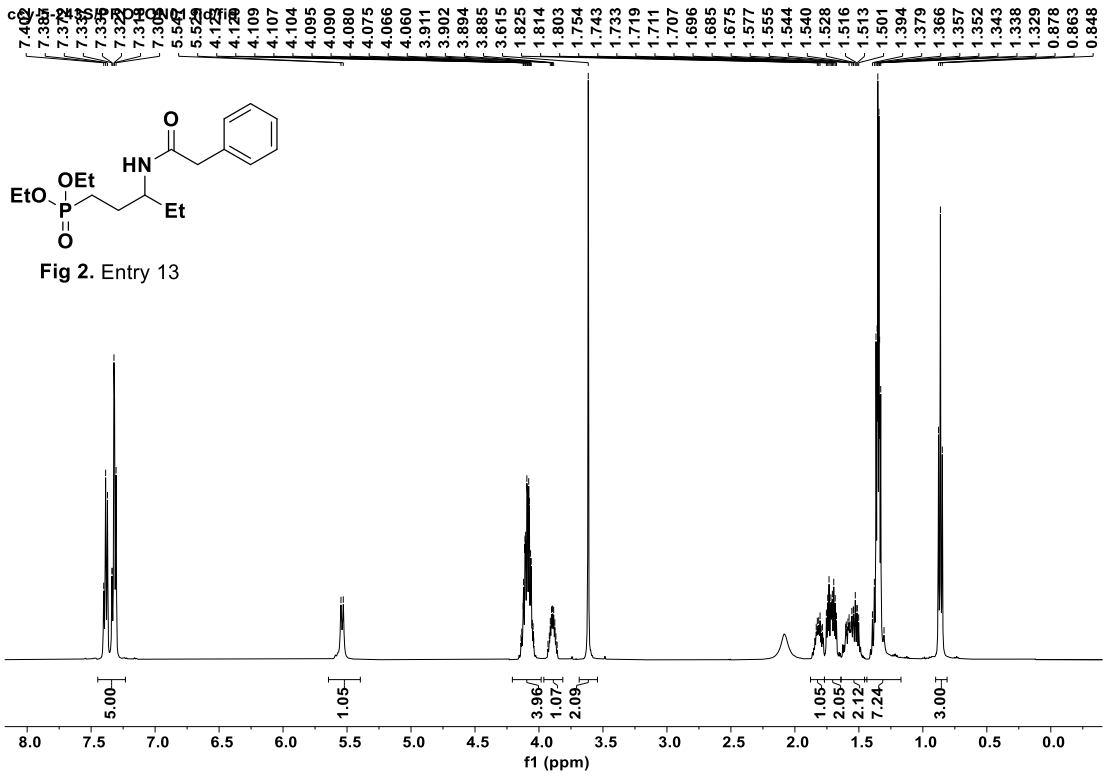


Fig 2. Entry 13

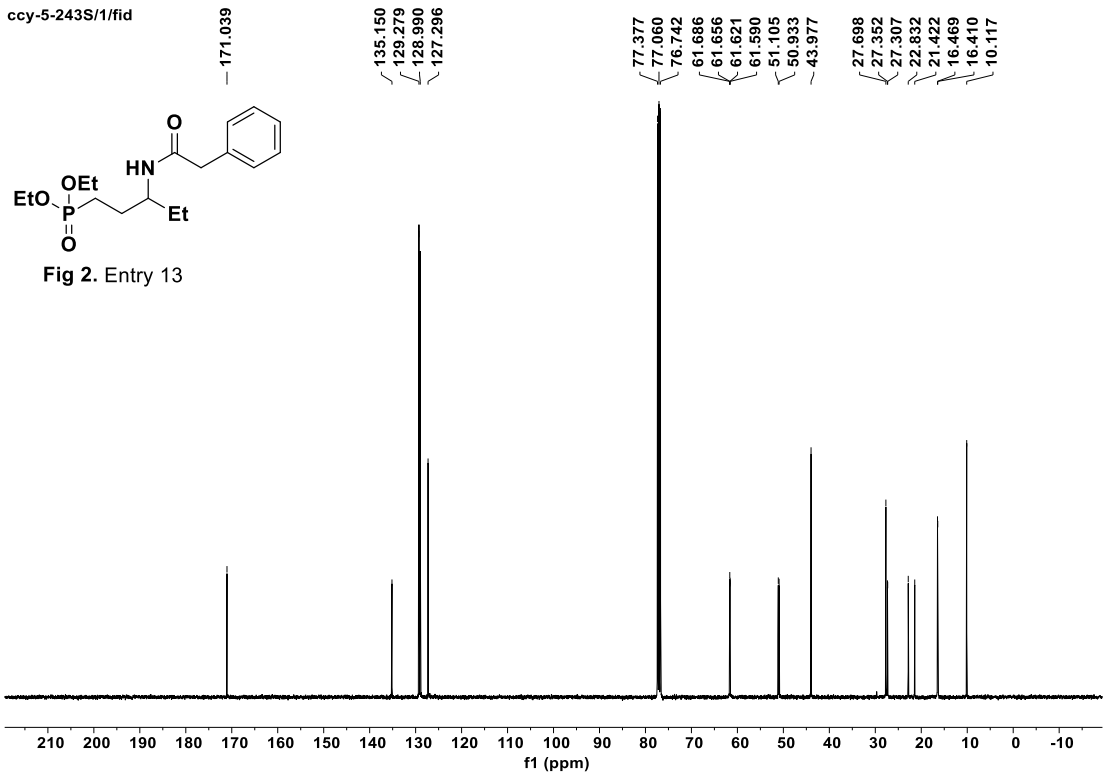


Fig 2. Entry 13

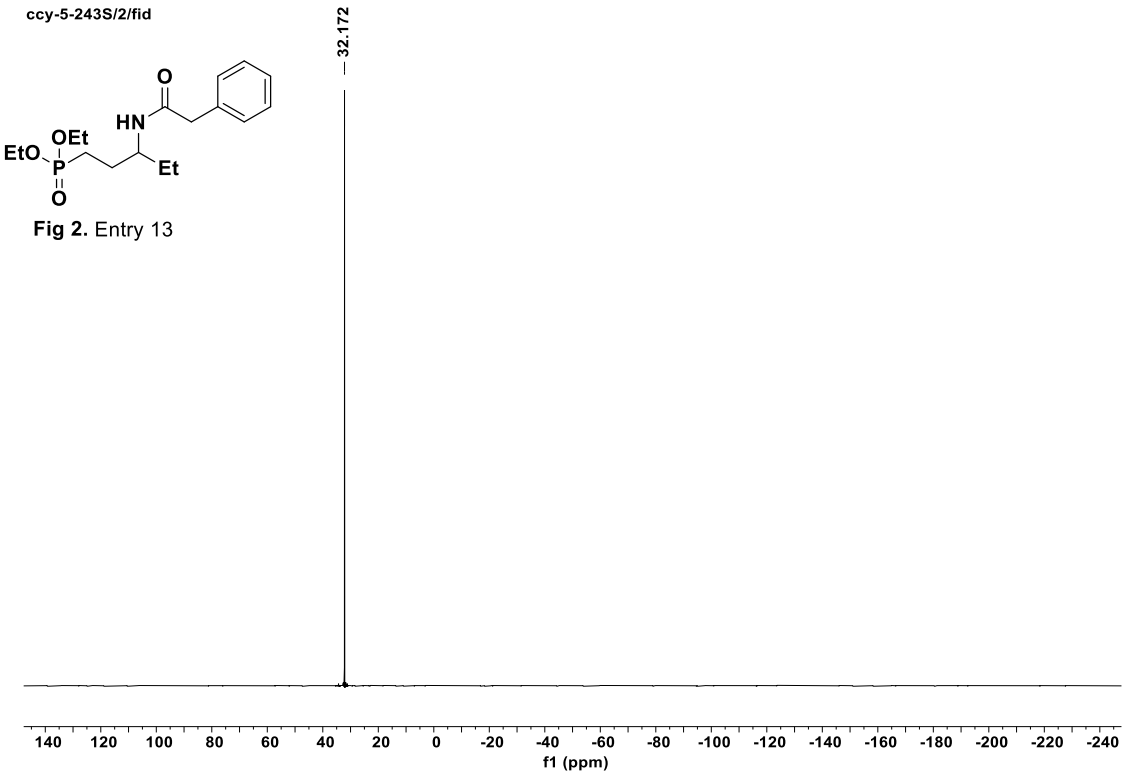
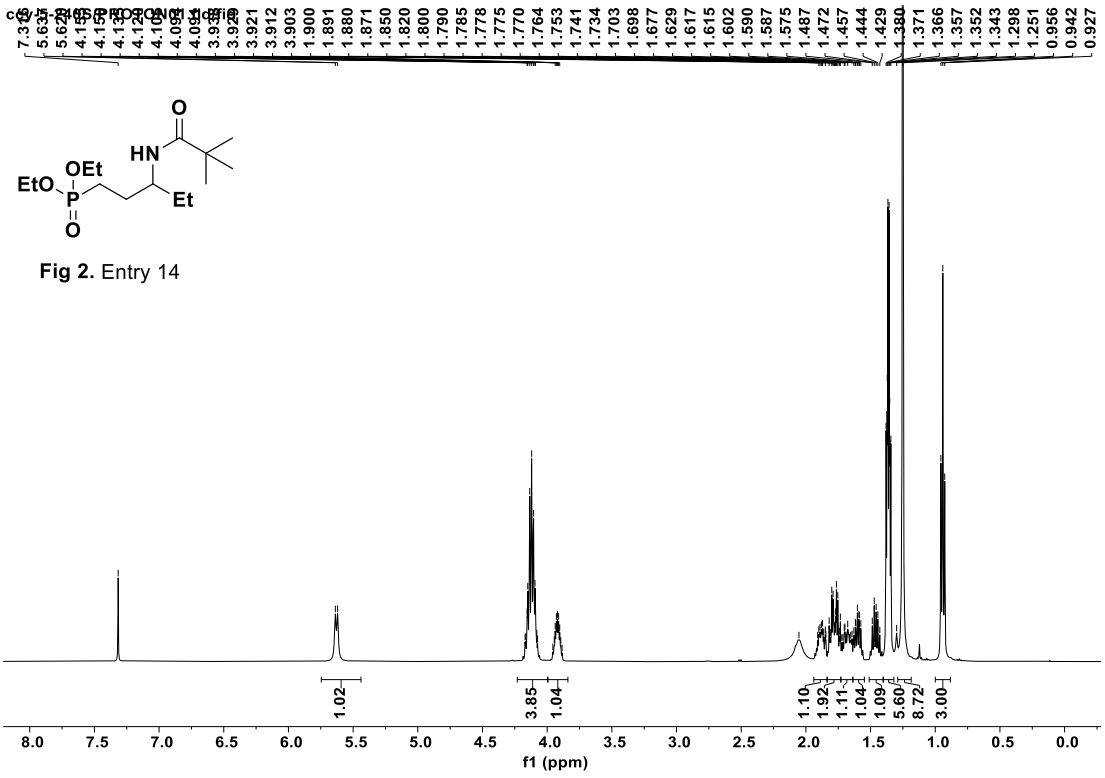


Fig 2. Entry 13



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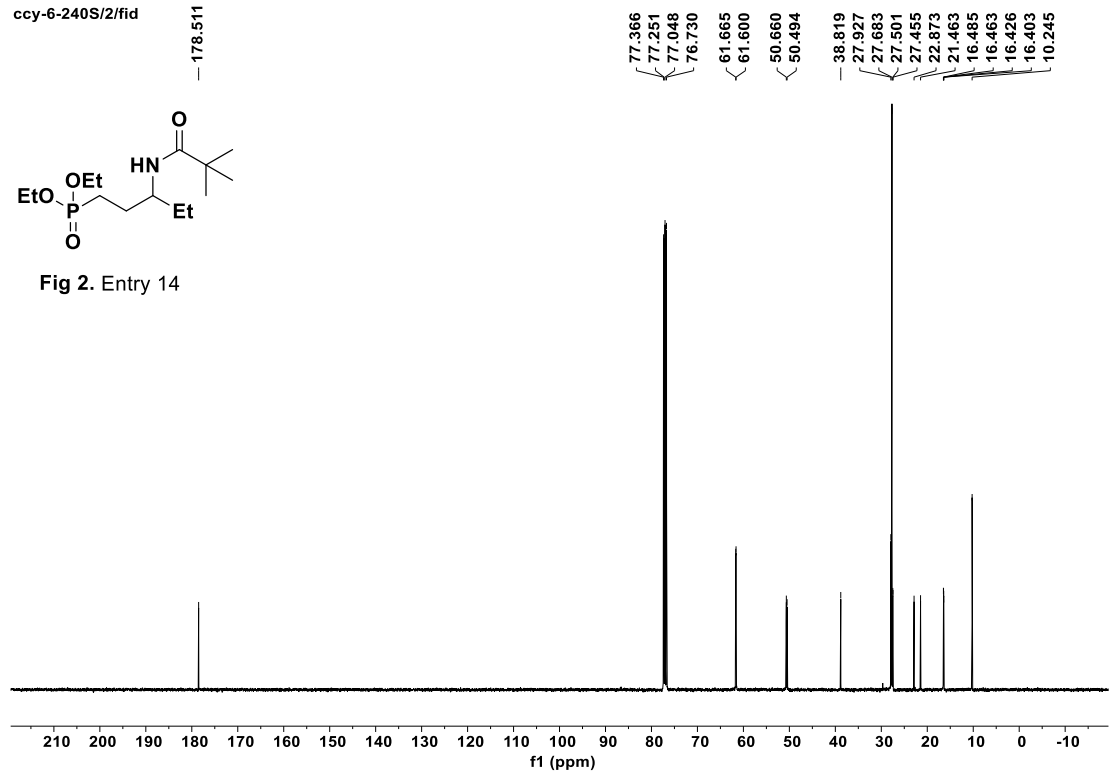

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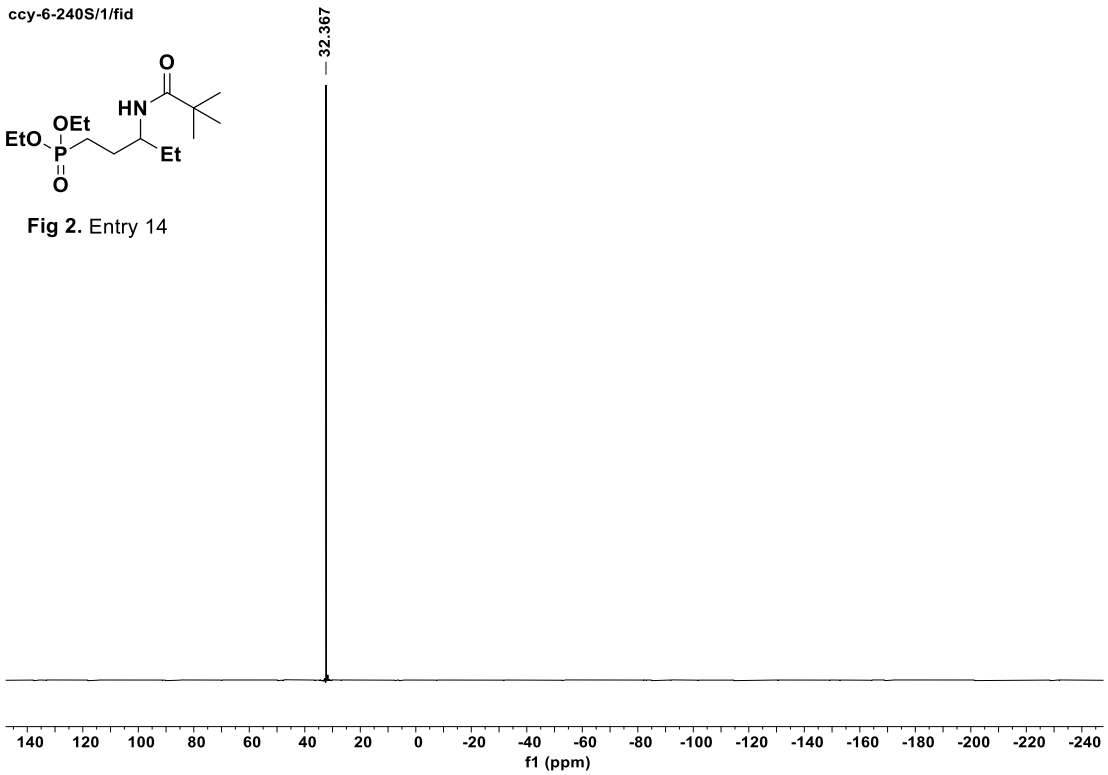

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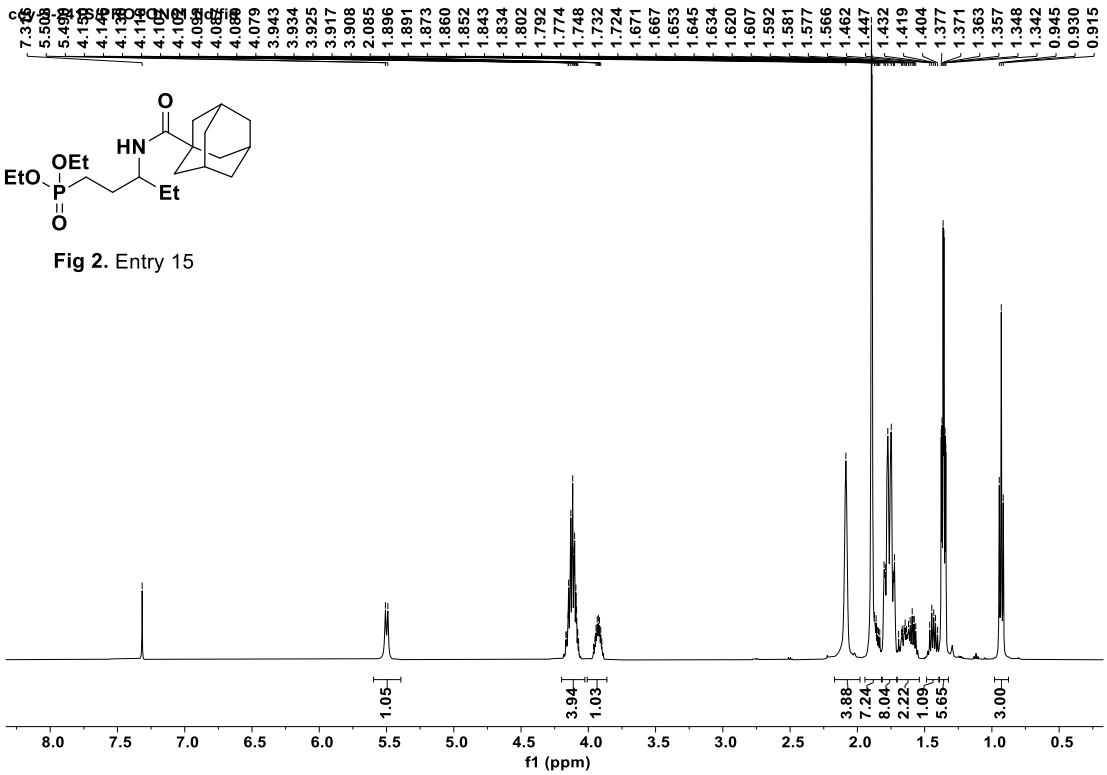

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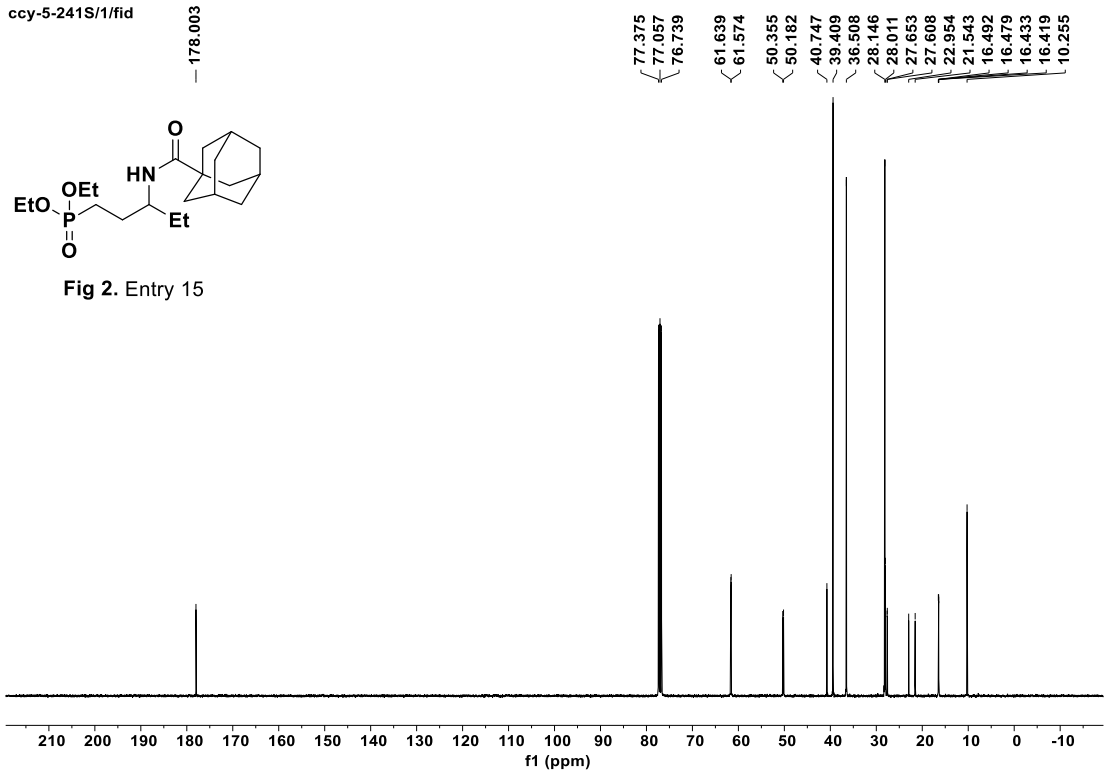

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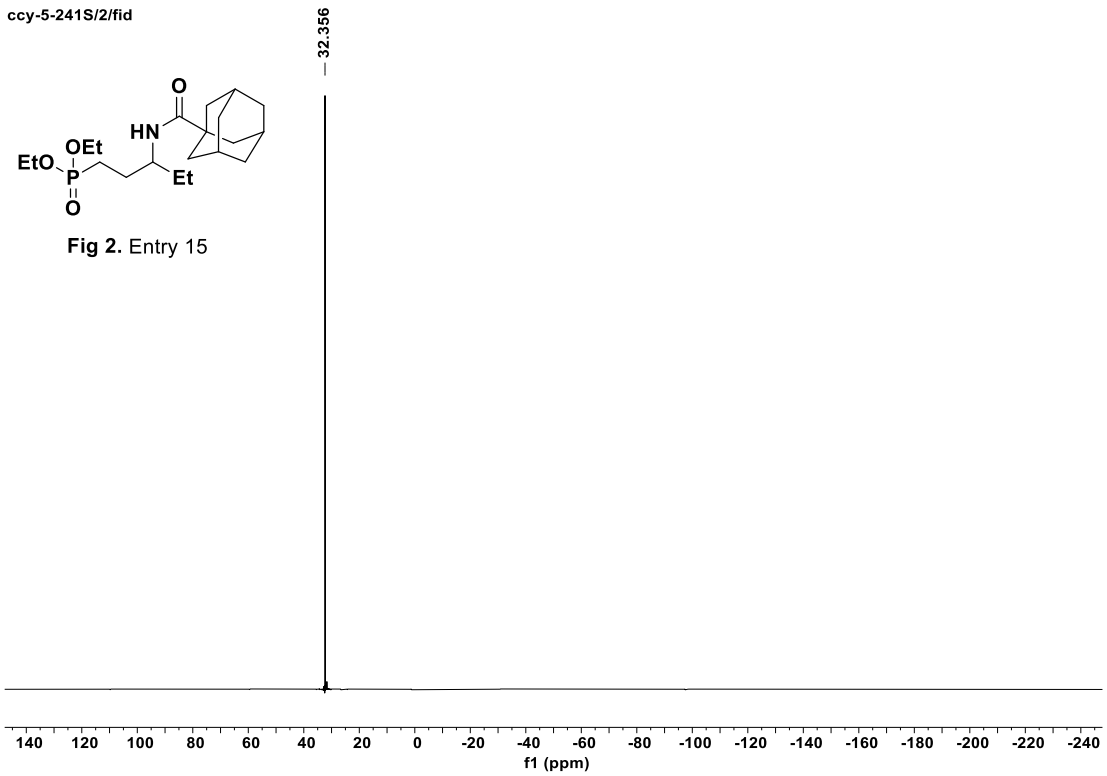

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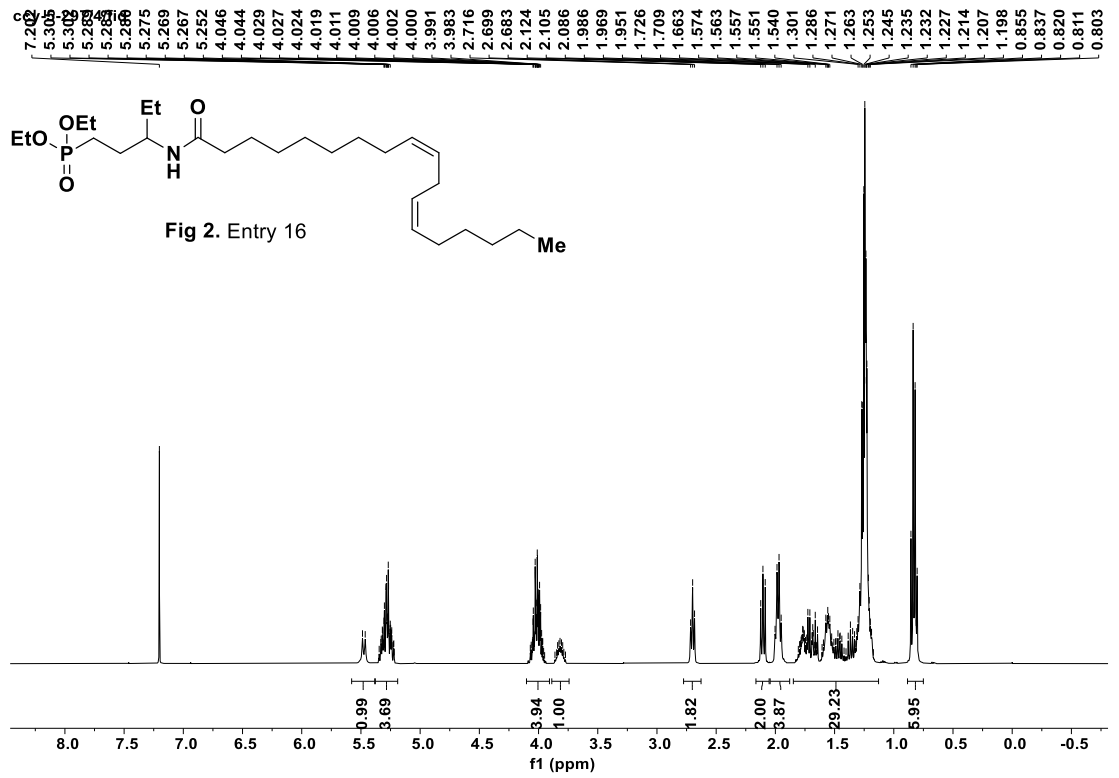

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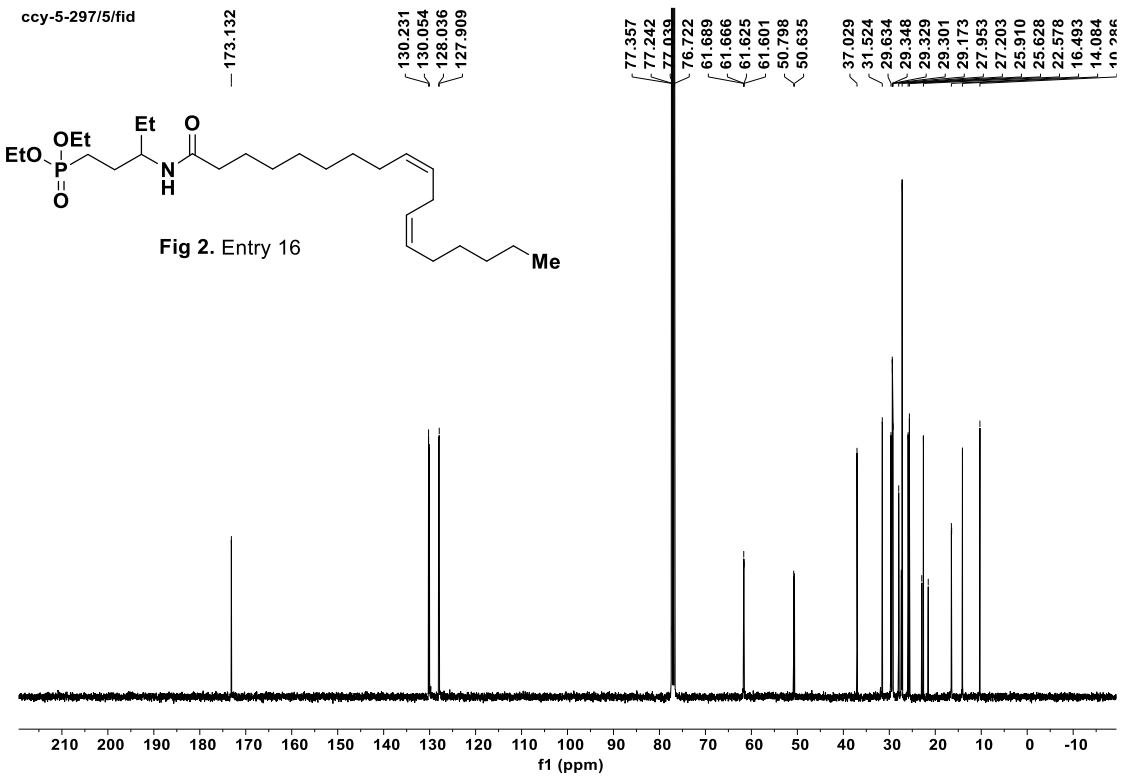

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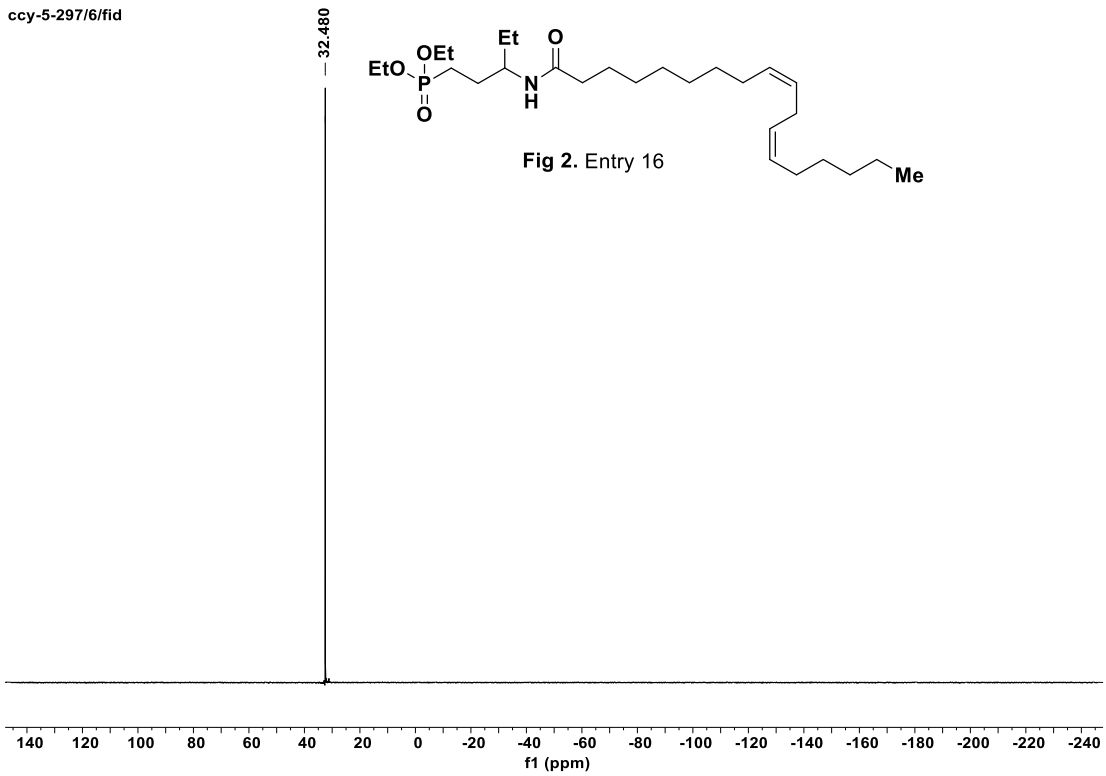

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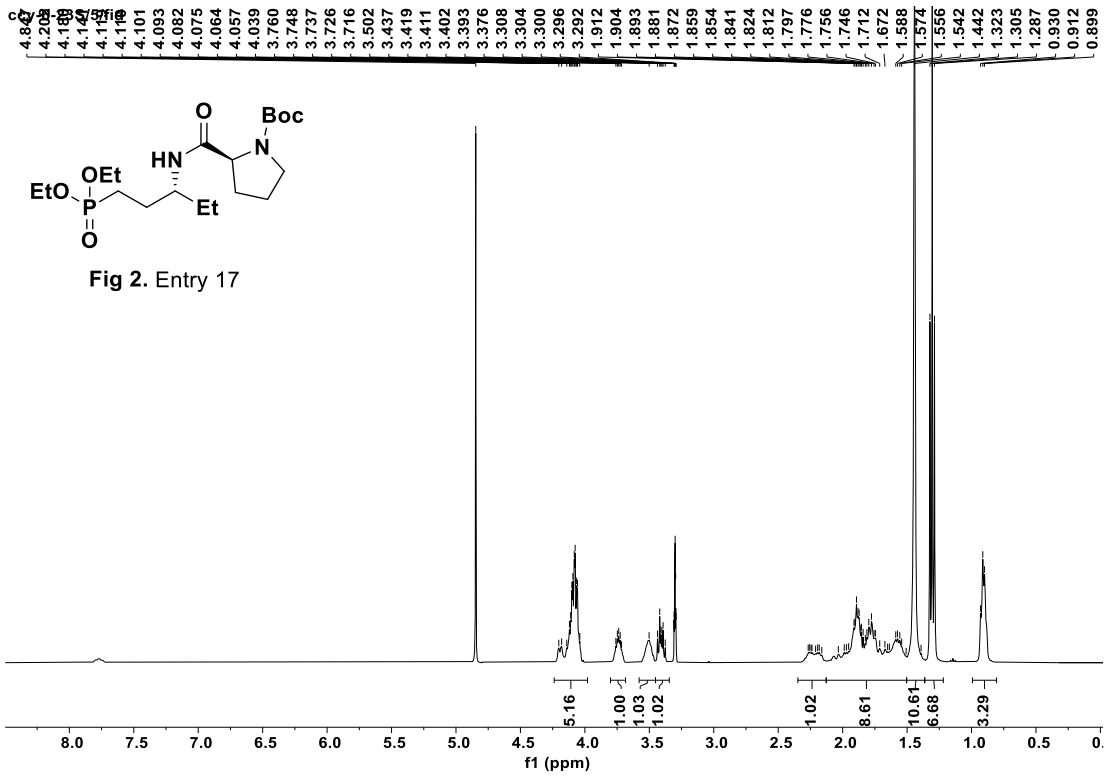

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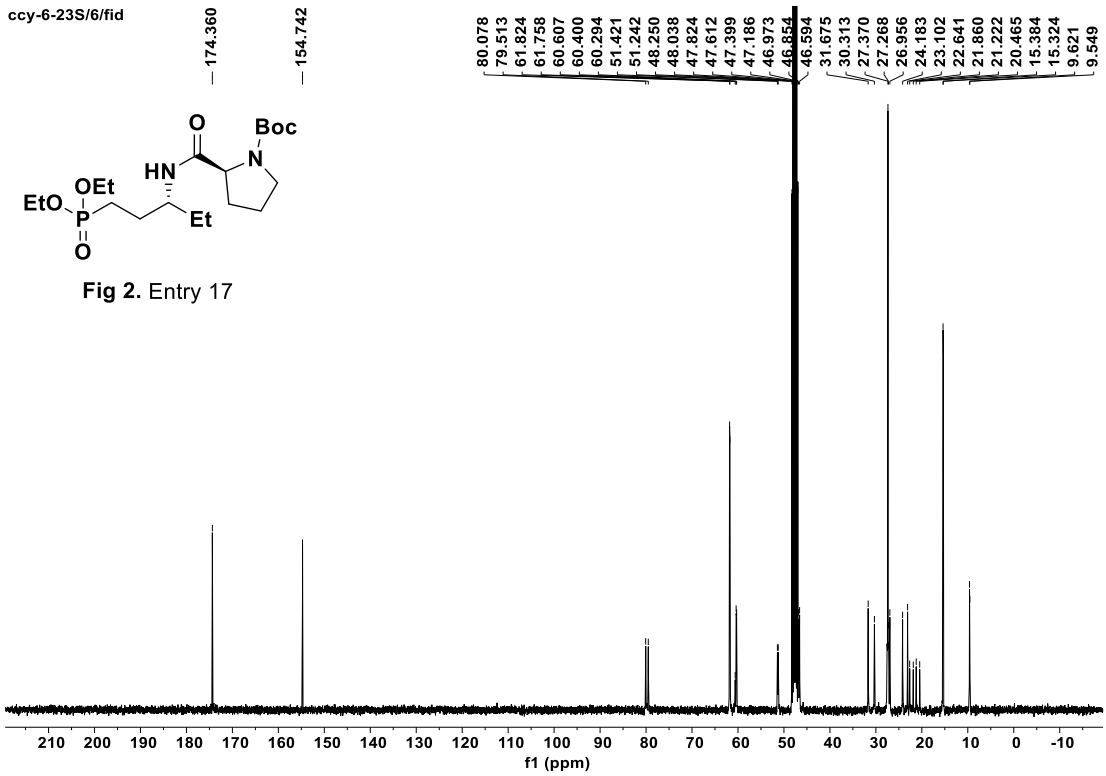

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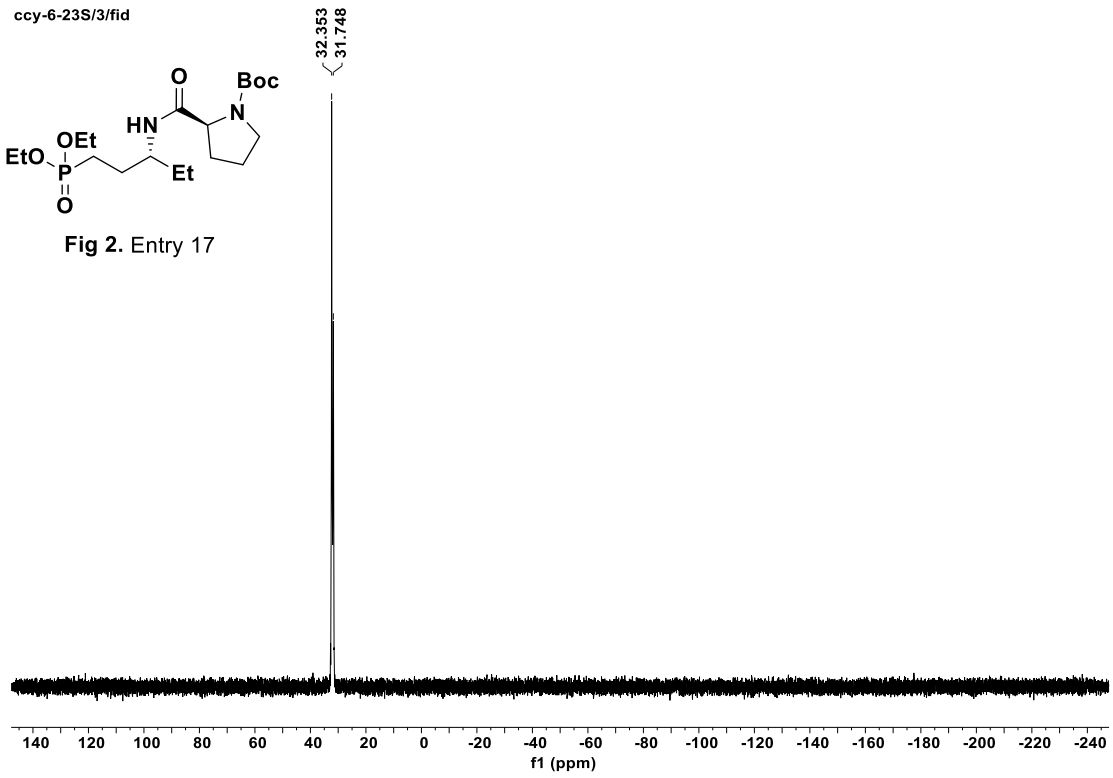

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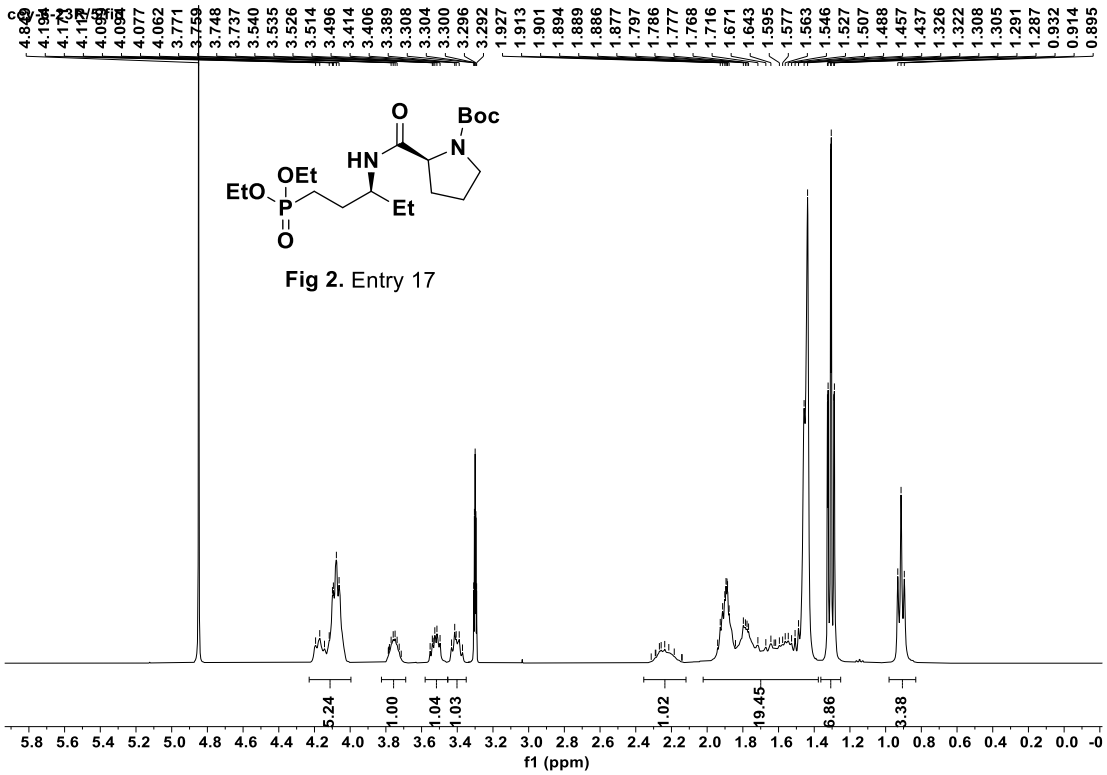

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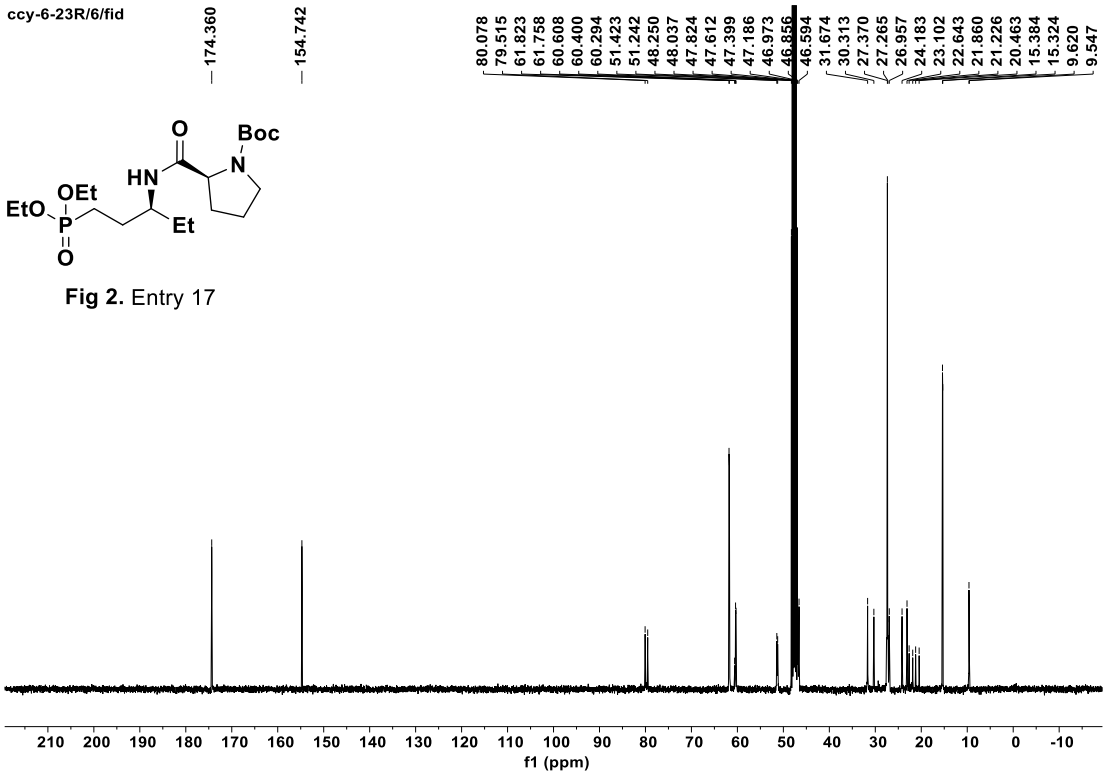

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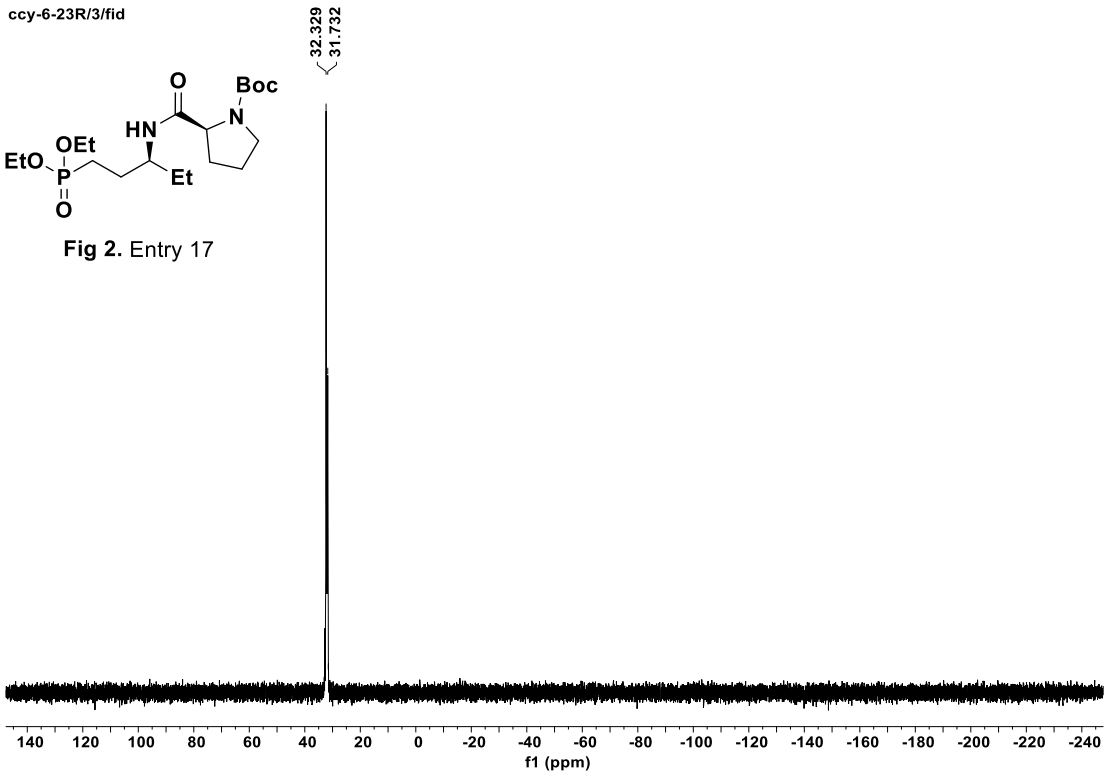

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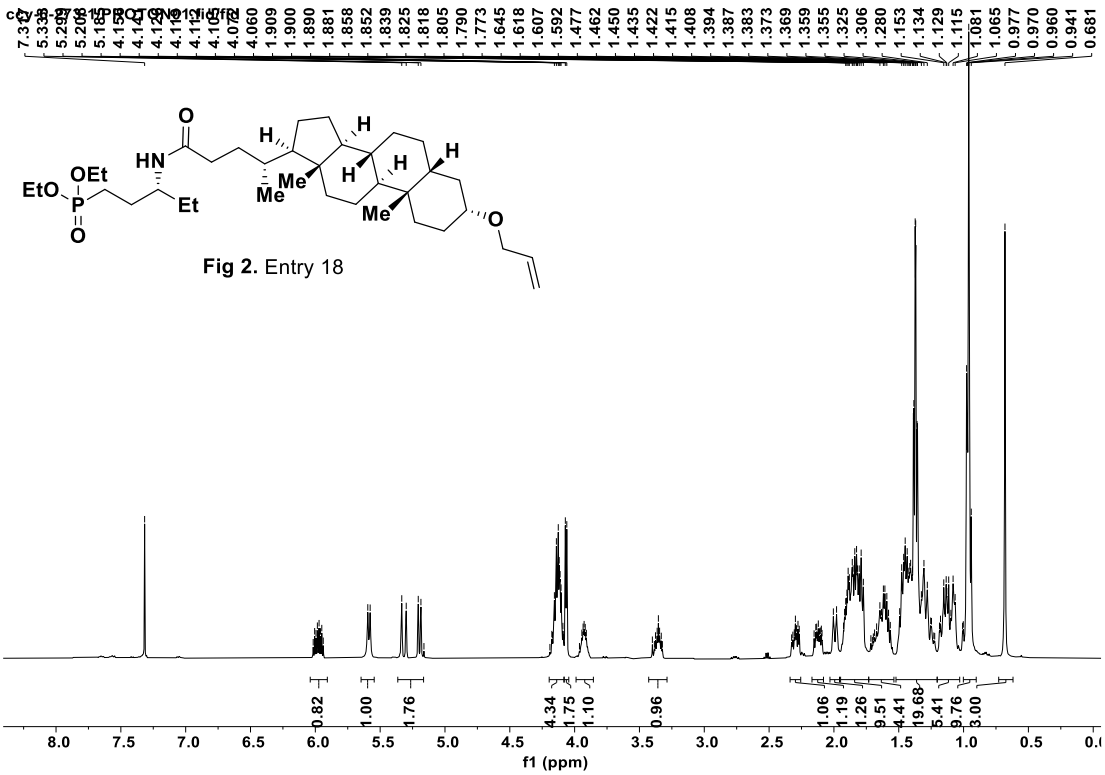

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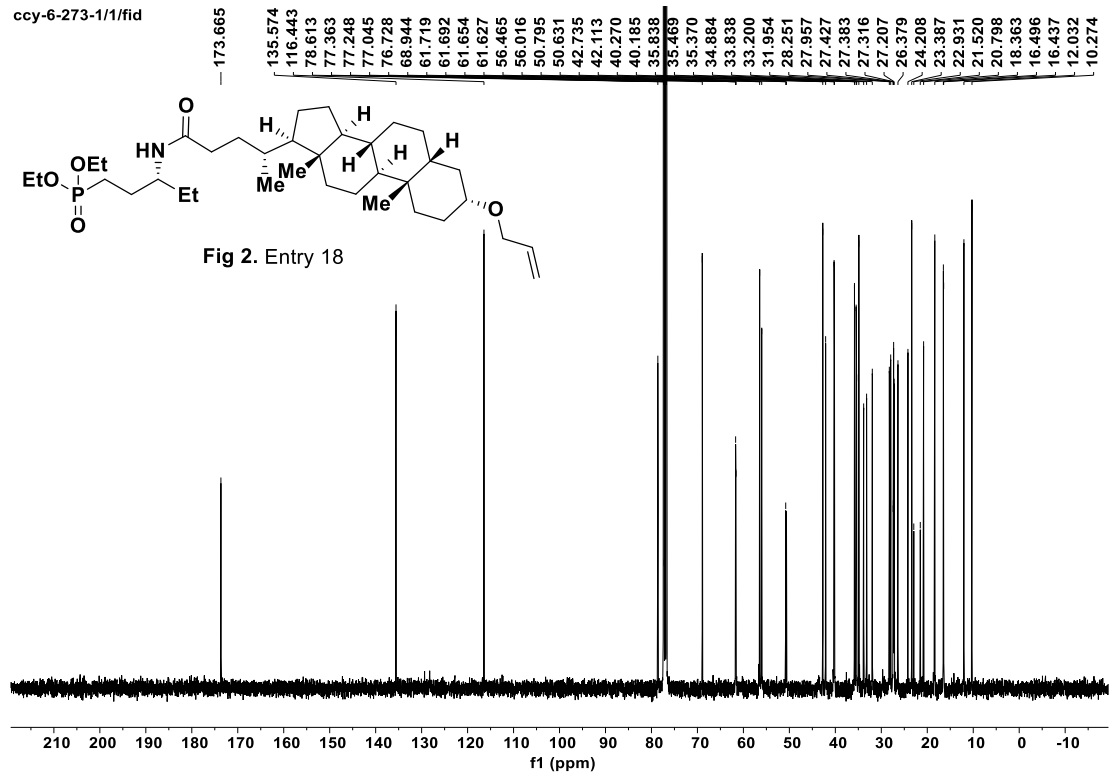

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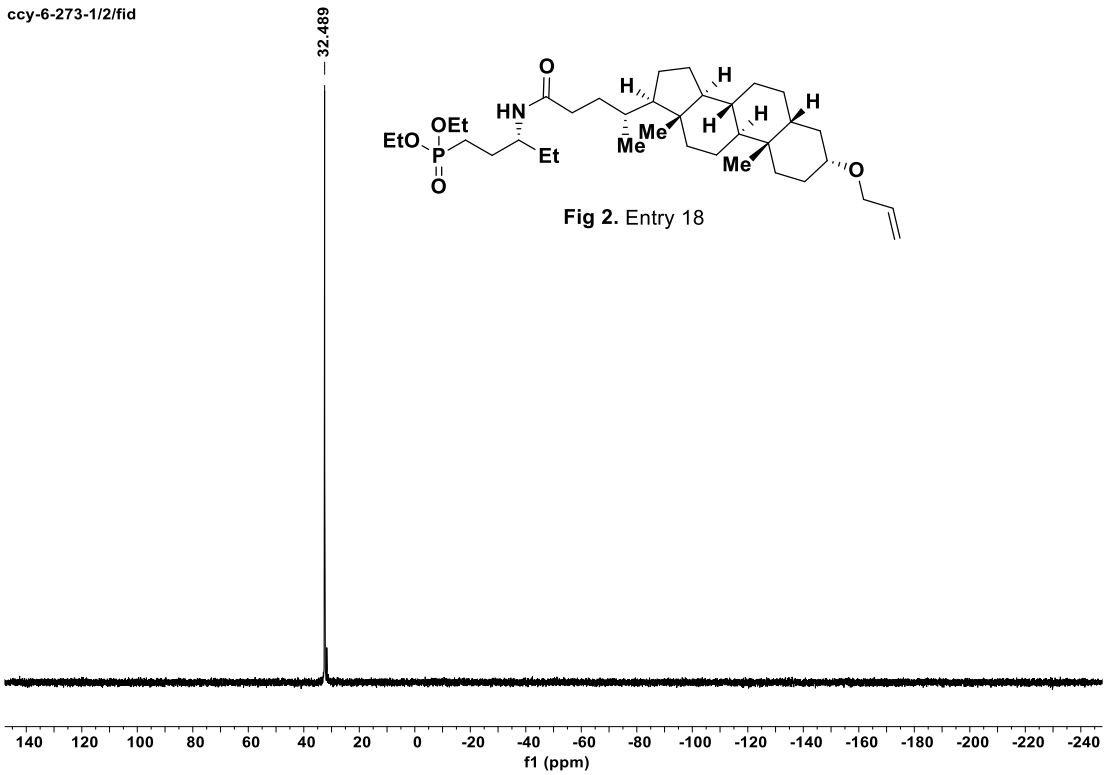

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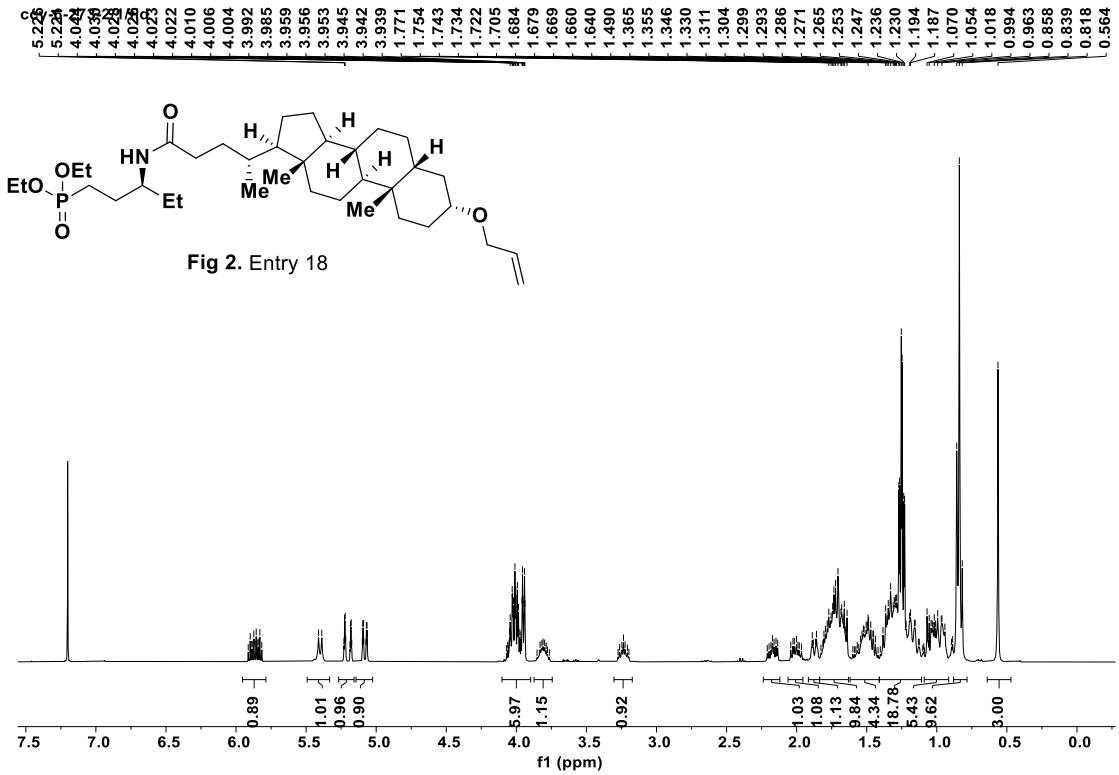

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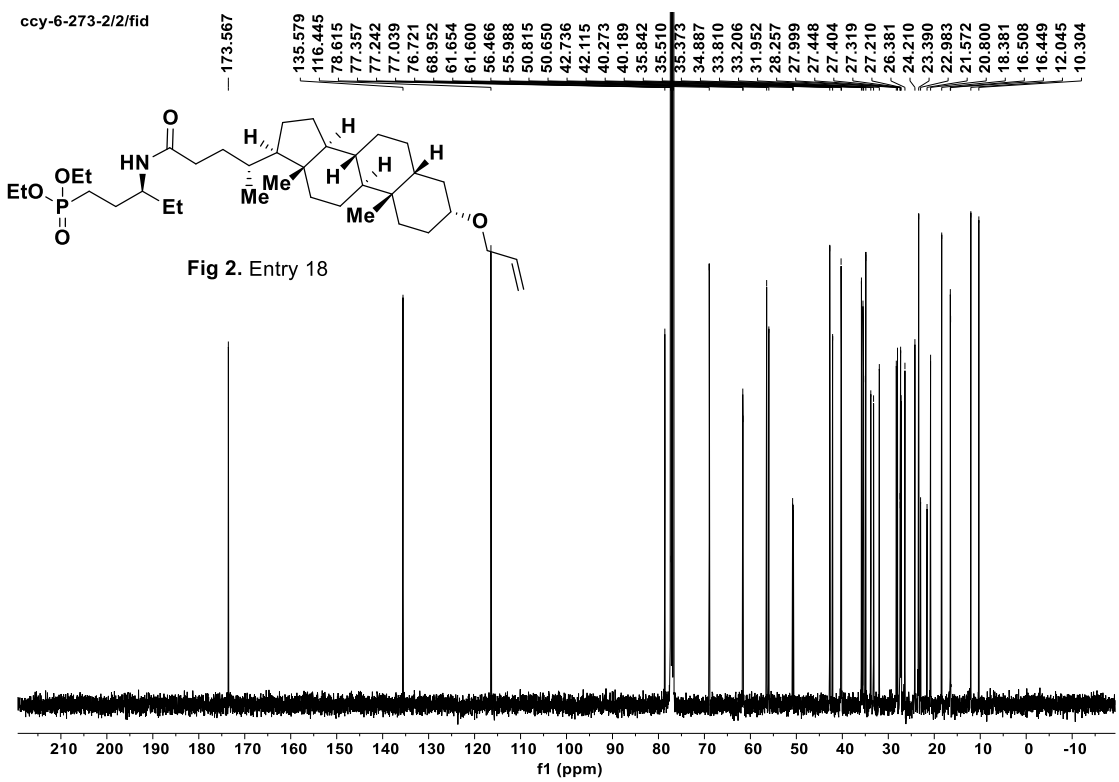

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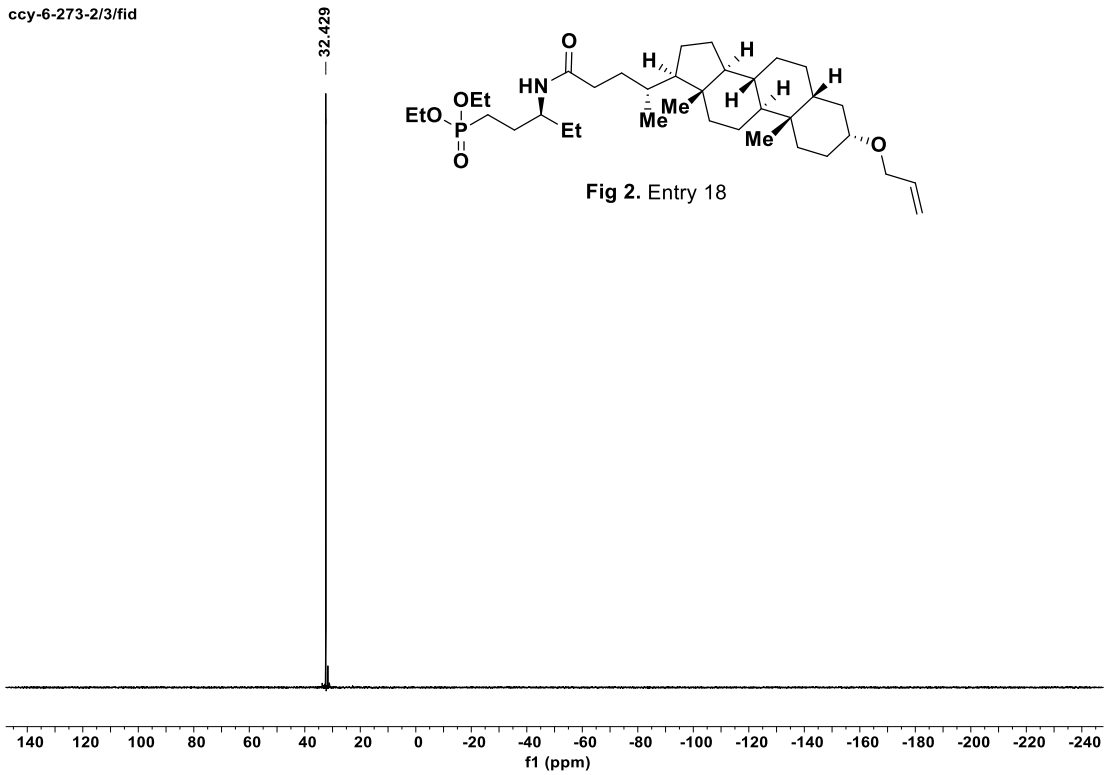

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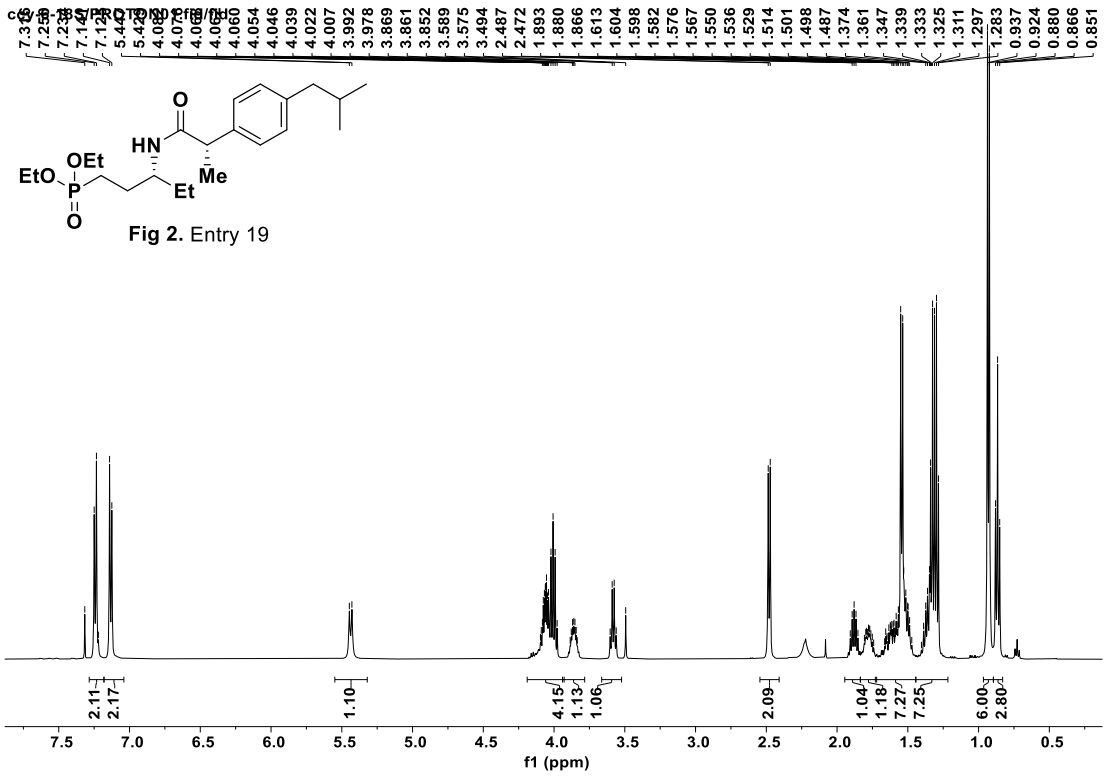

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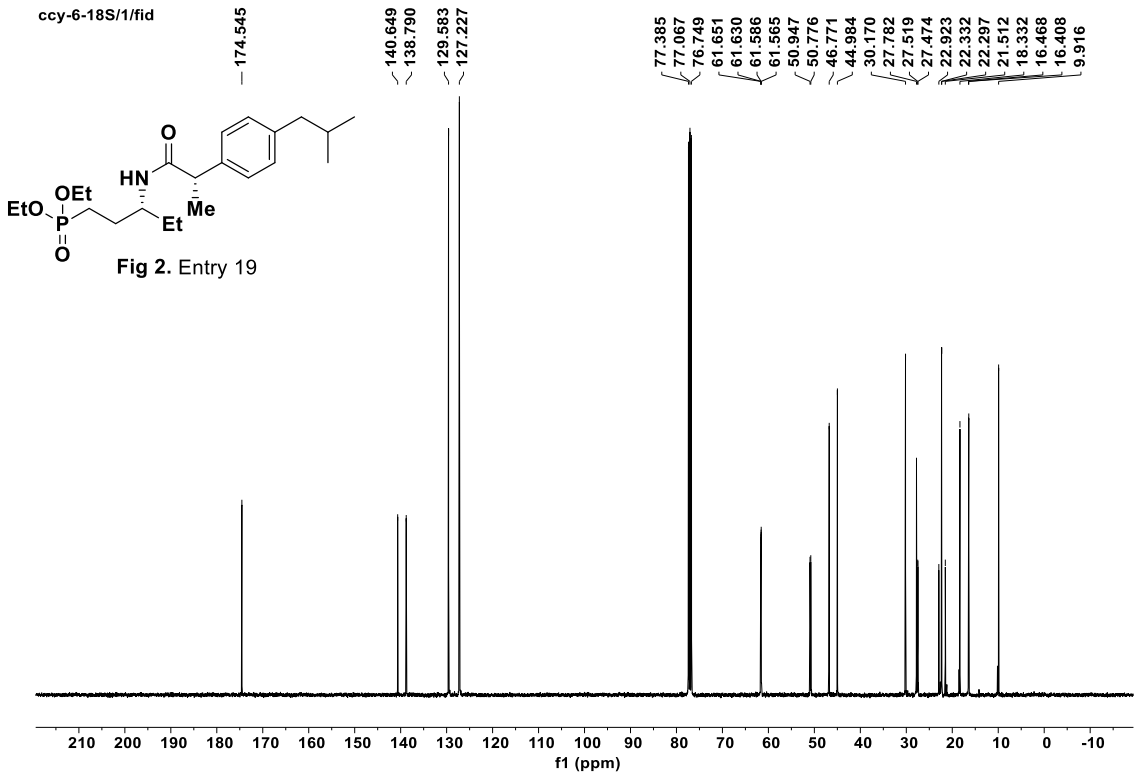

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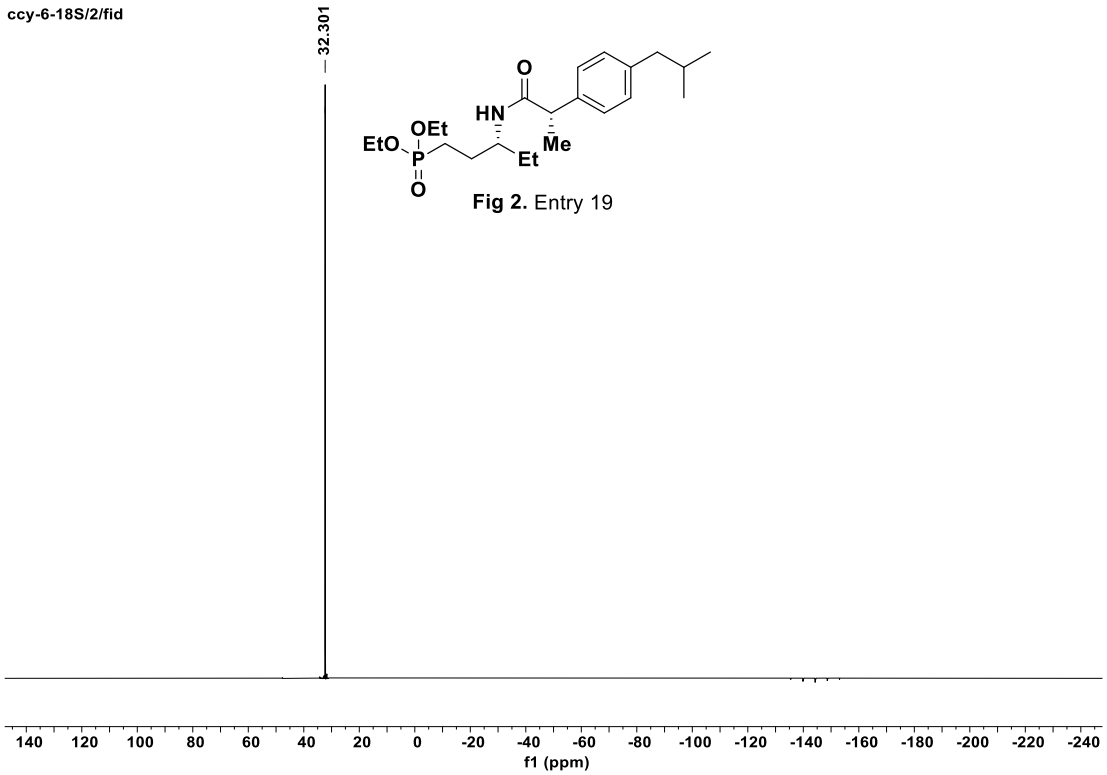

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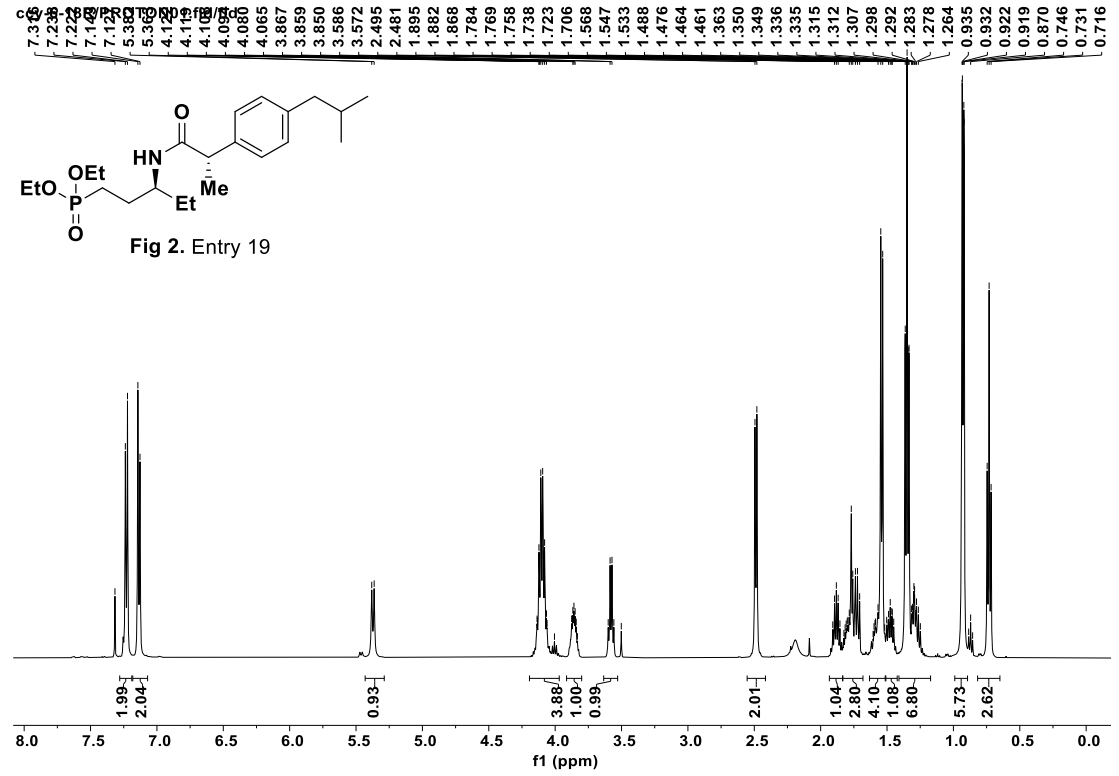

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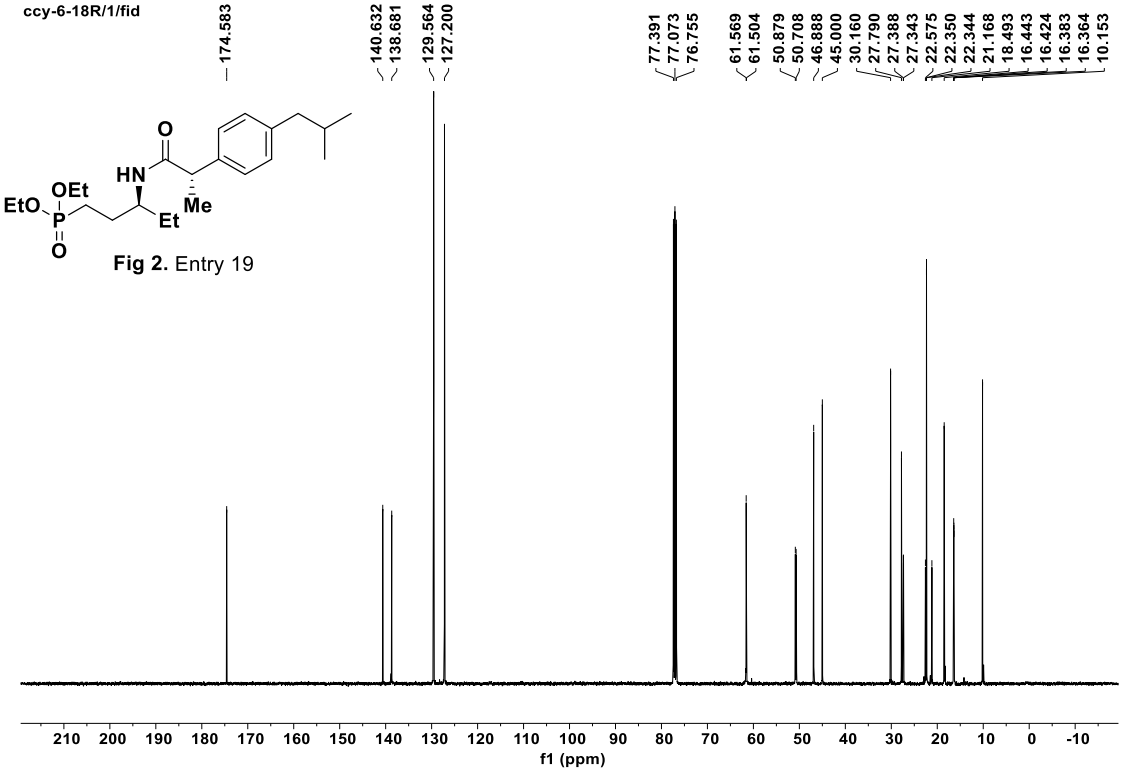

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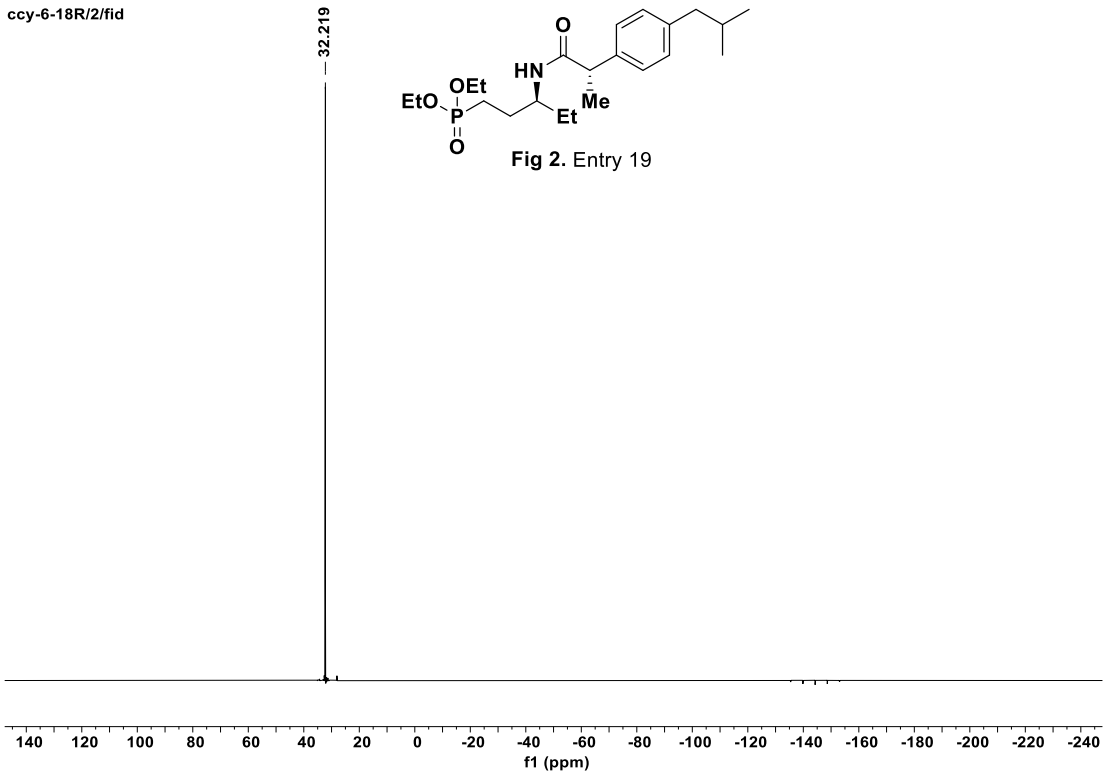

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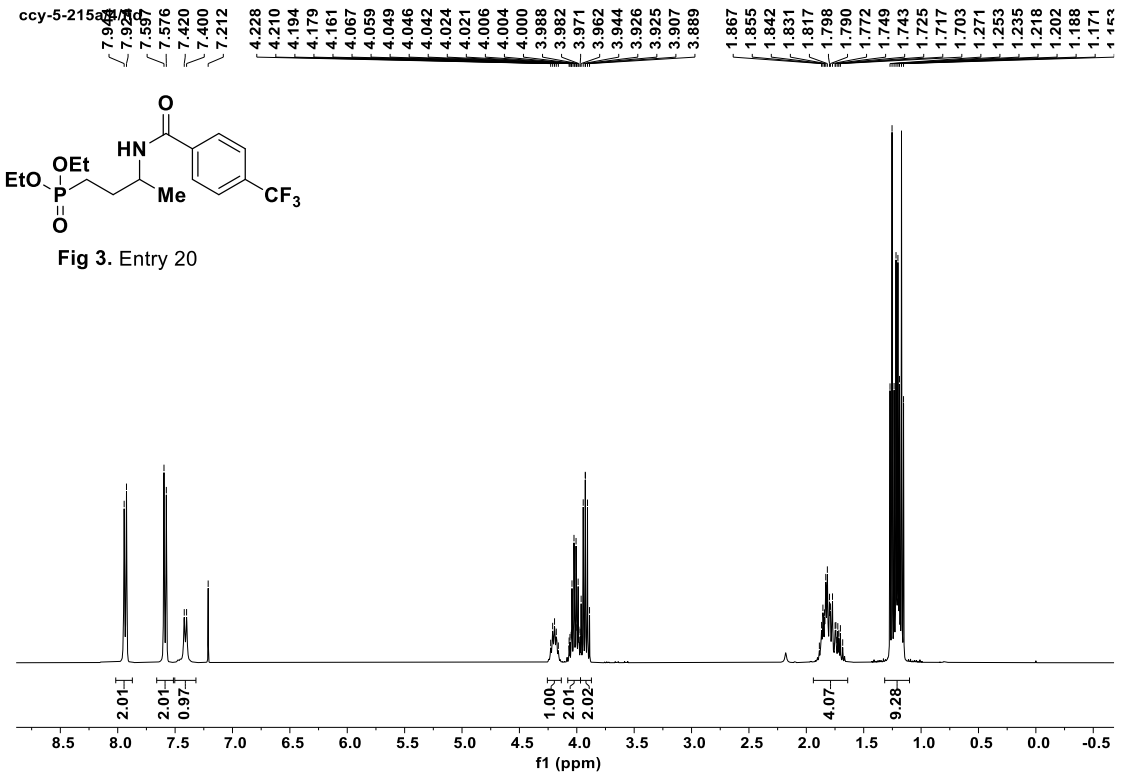

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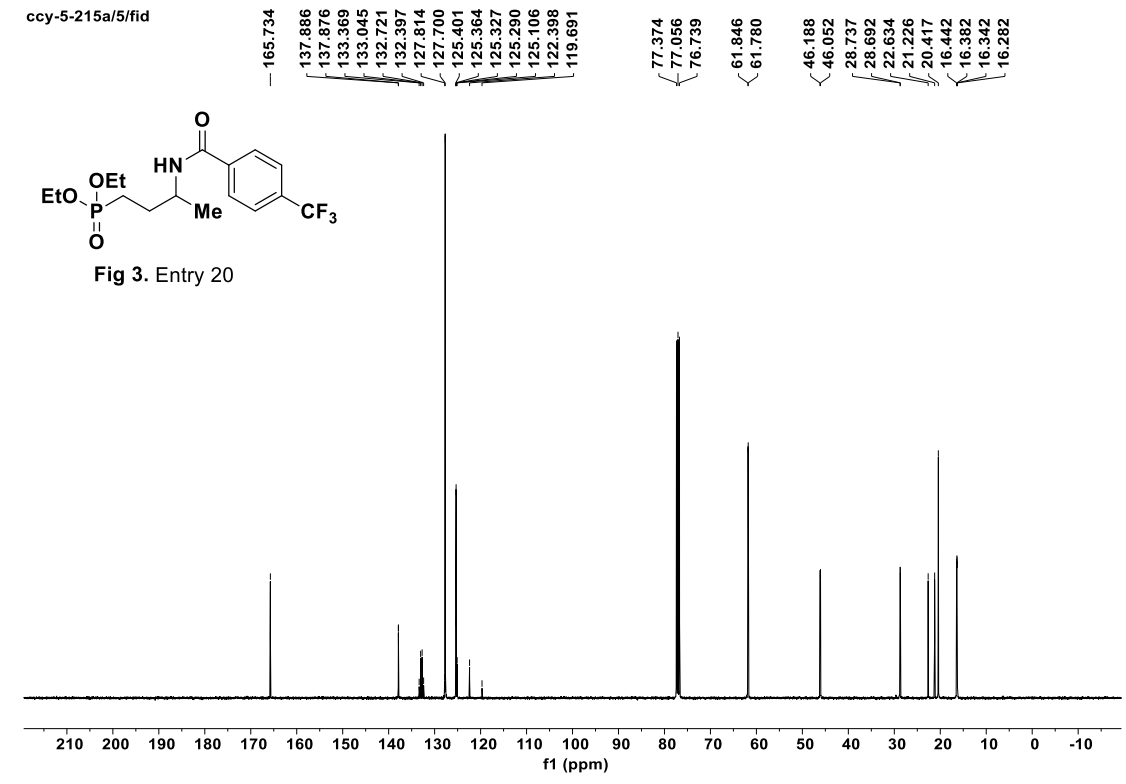


Fig 3. Entry 20

ccy-5-215/3/fid

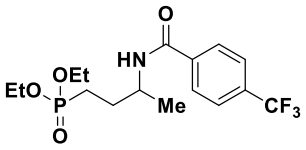
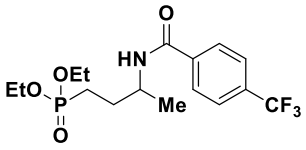


Fig 3. Entry 20

ccy-5-215/FLUORINE01.fid/fid



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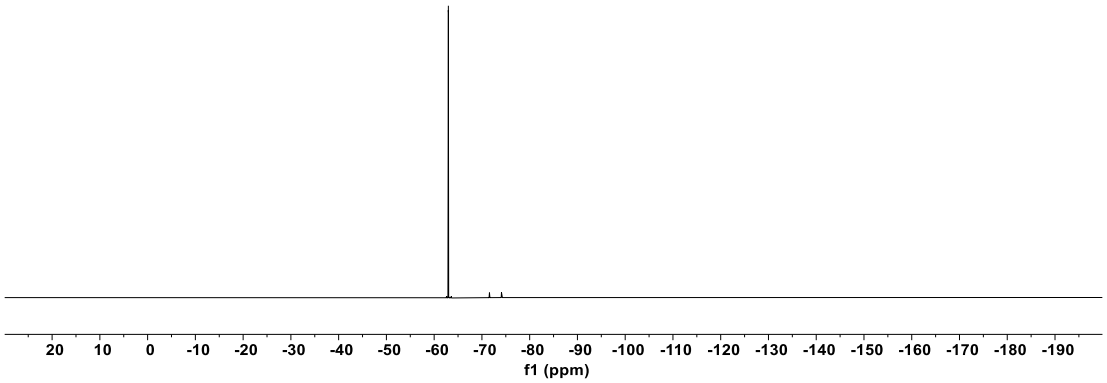

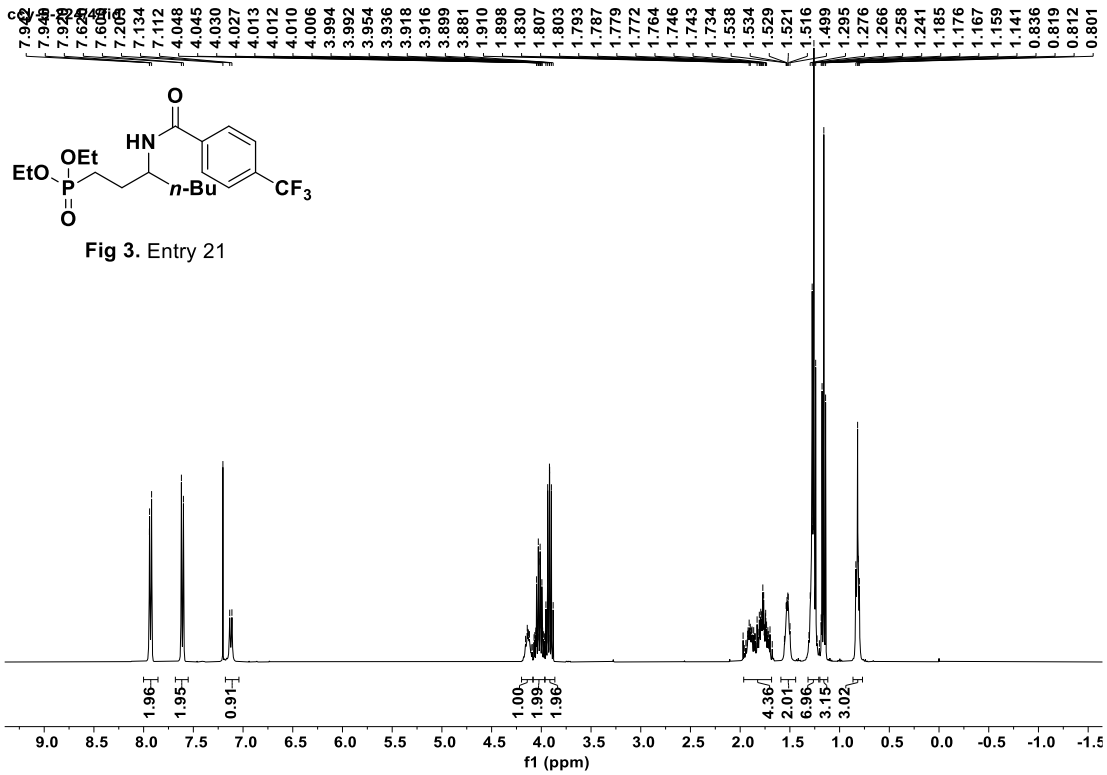

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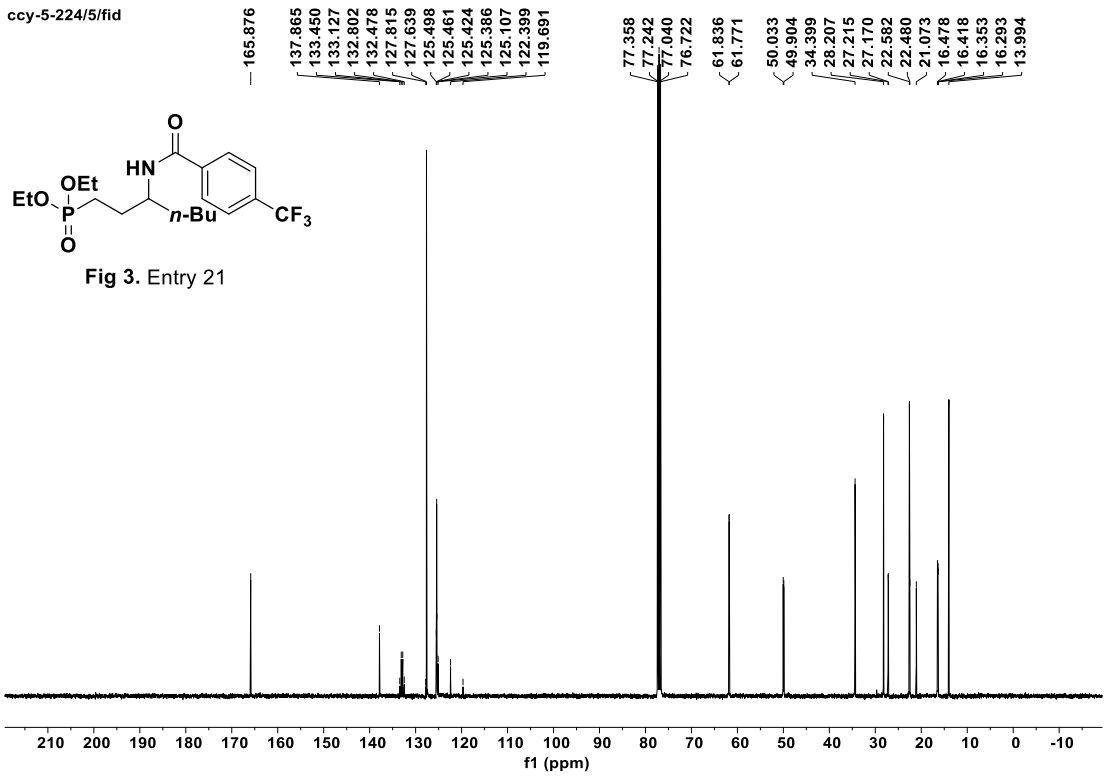

Fig 3. Entry 21

ccy-5-224/6/fid

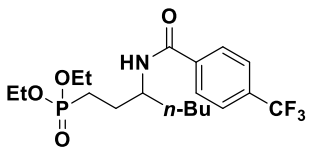

Fig 3. Entry 21

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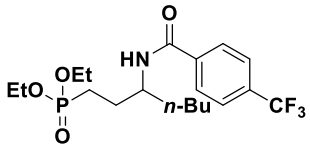

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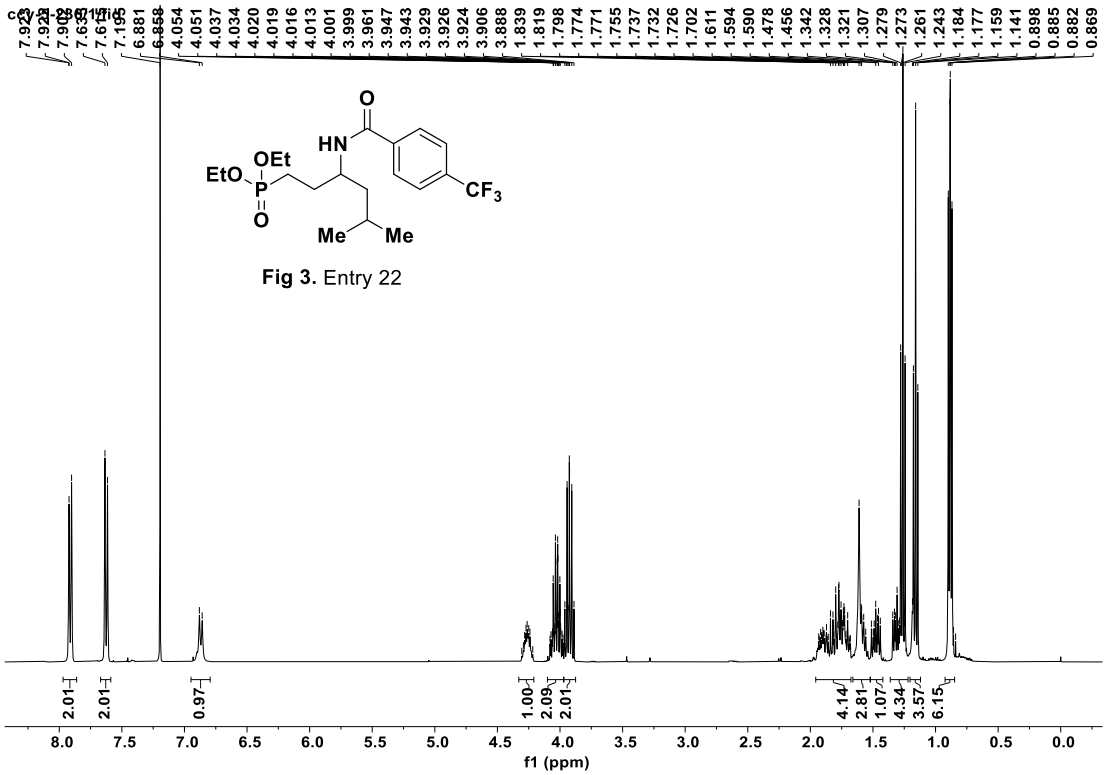

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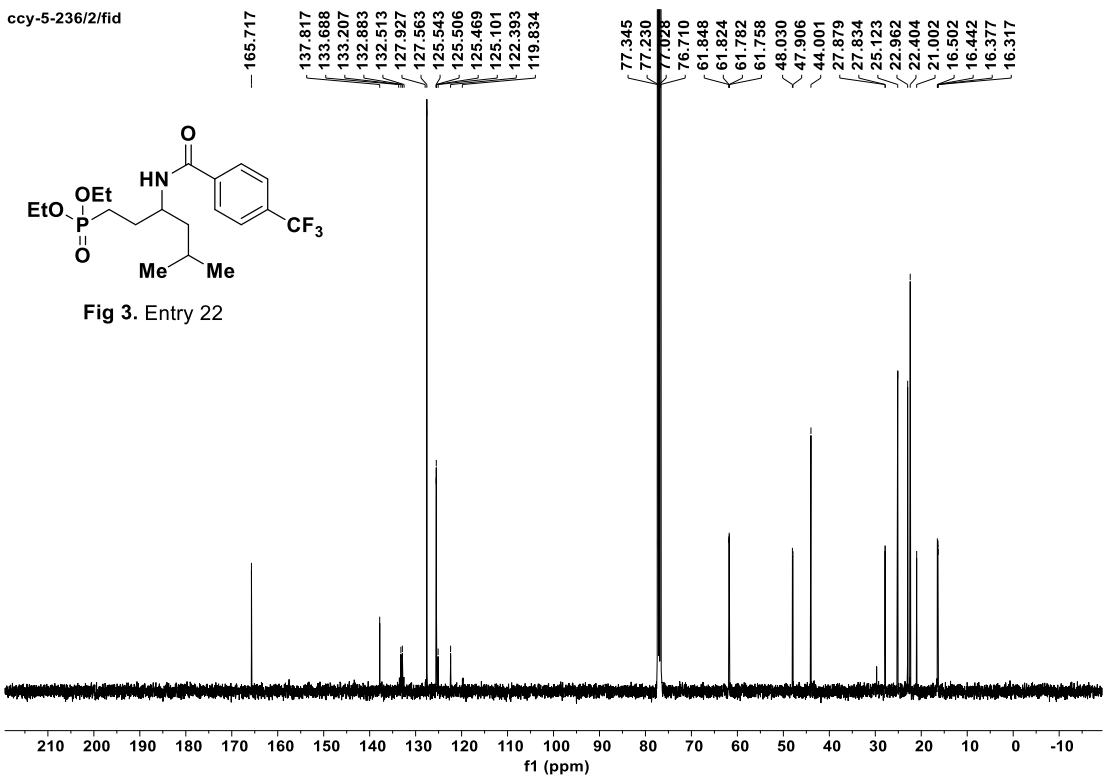

Fig 3. Entry 22

ccy-5-236S/3/fid

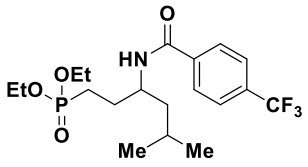

Fig 3. Entry 22

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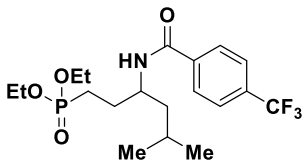

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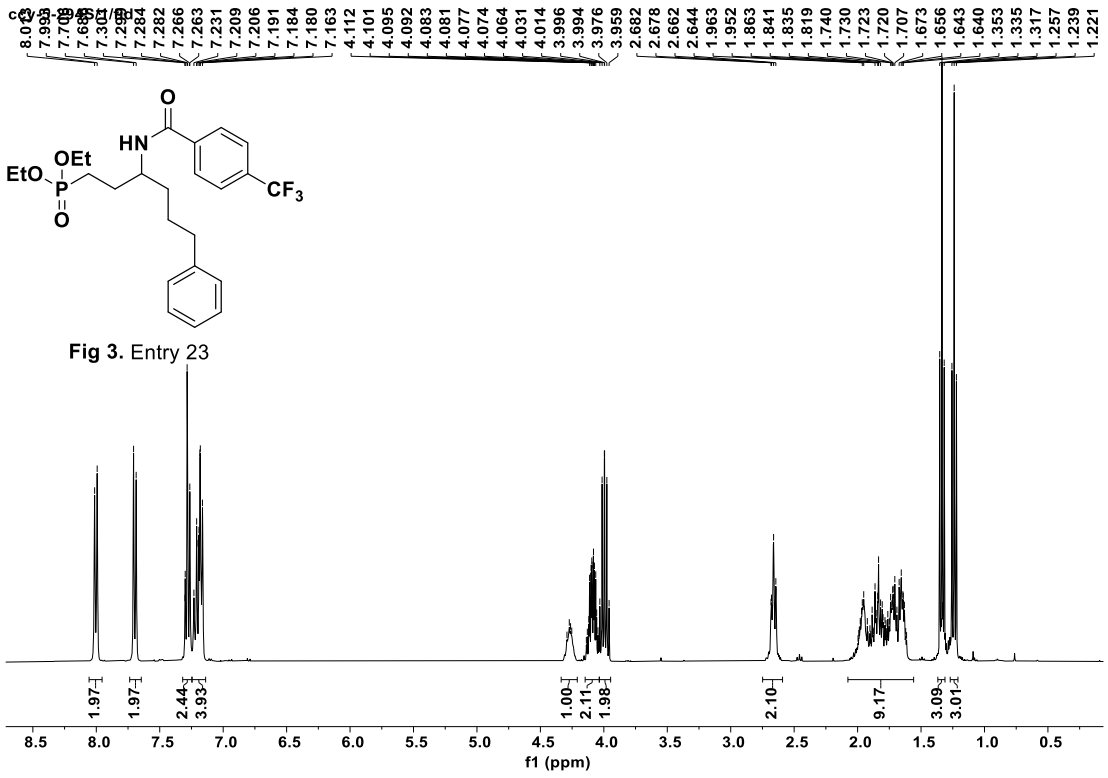

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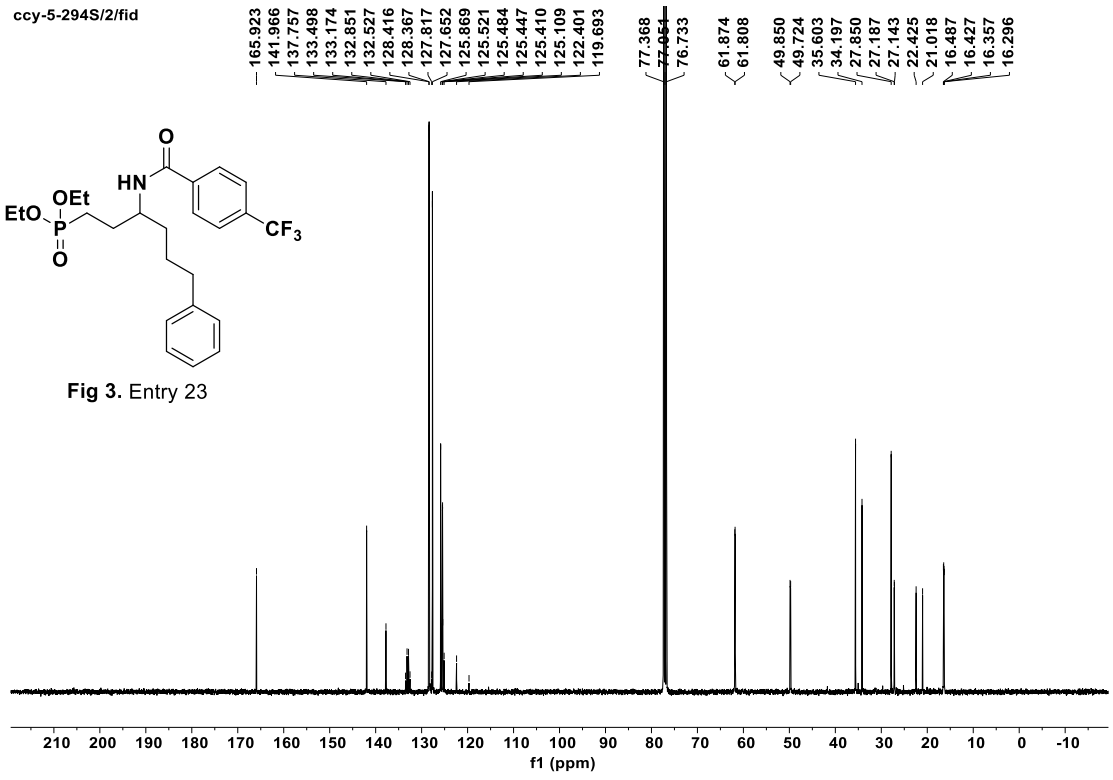

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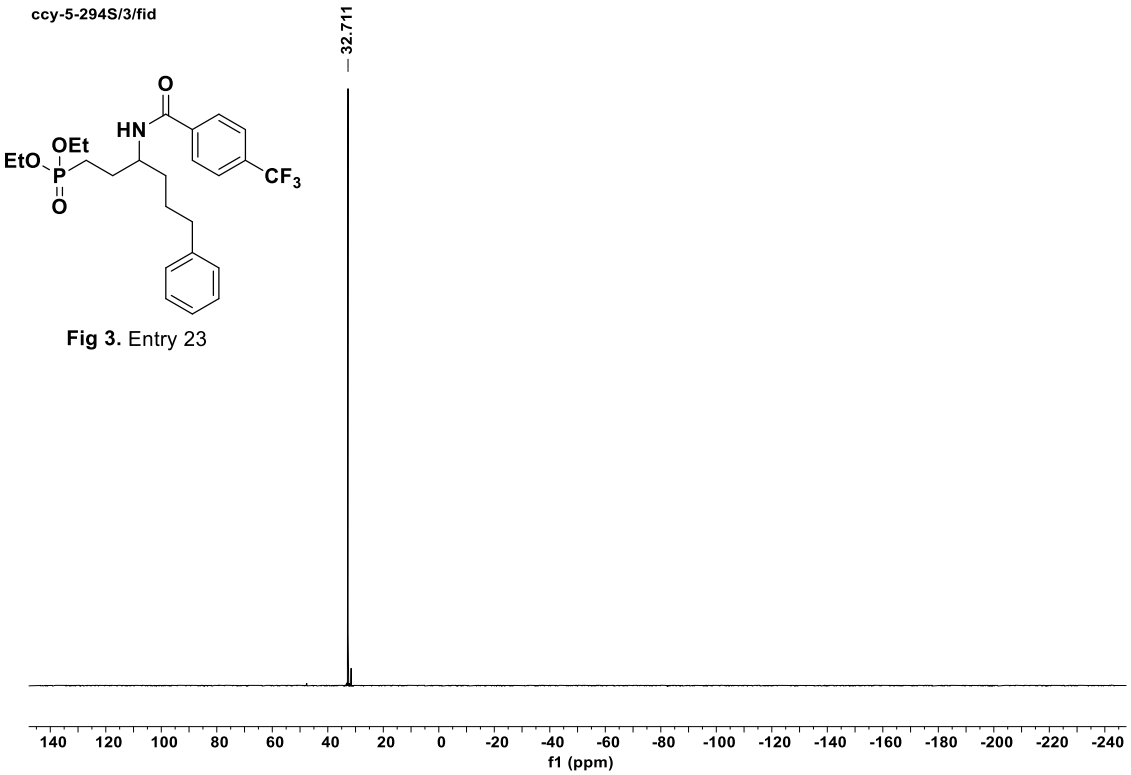

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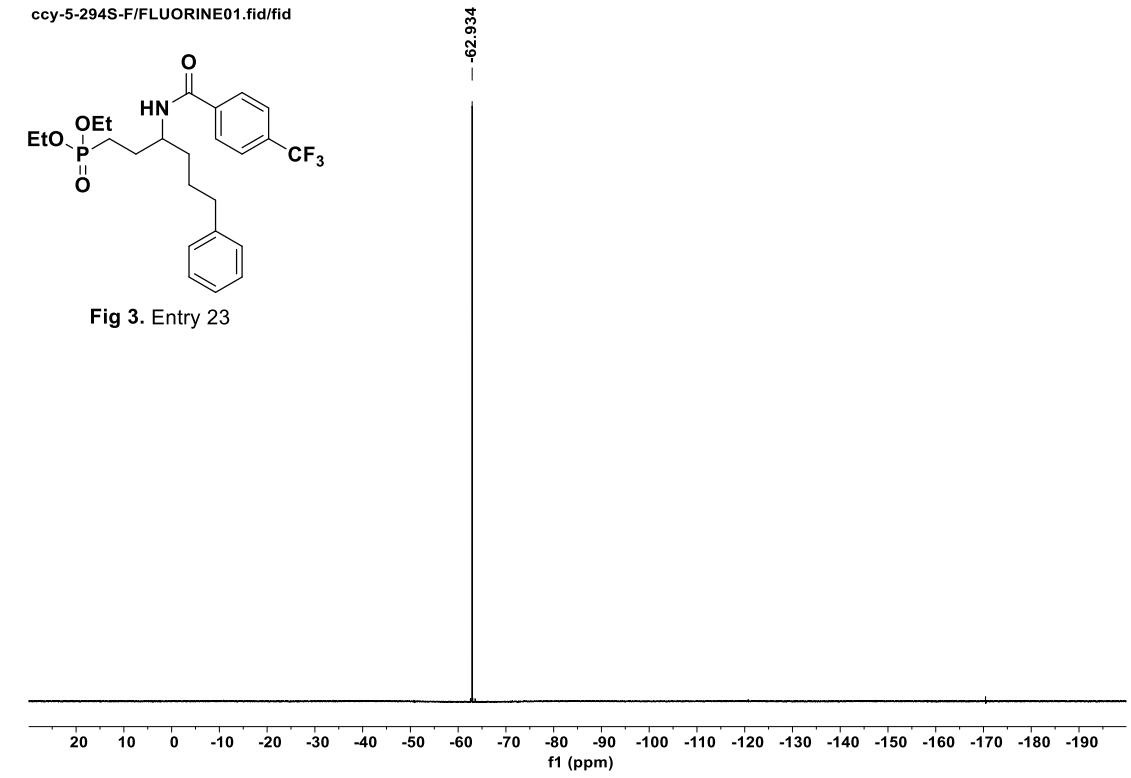

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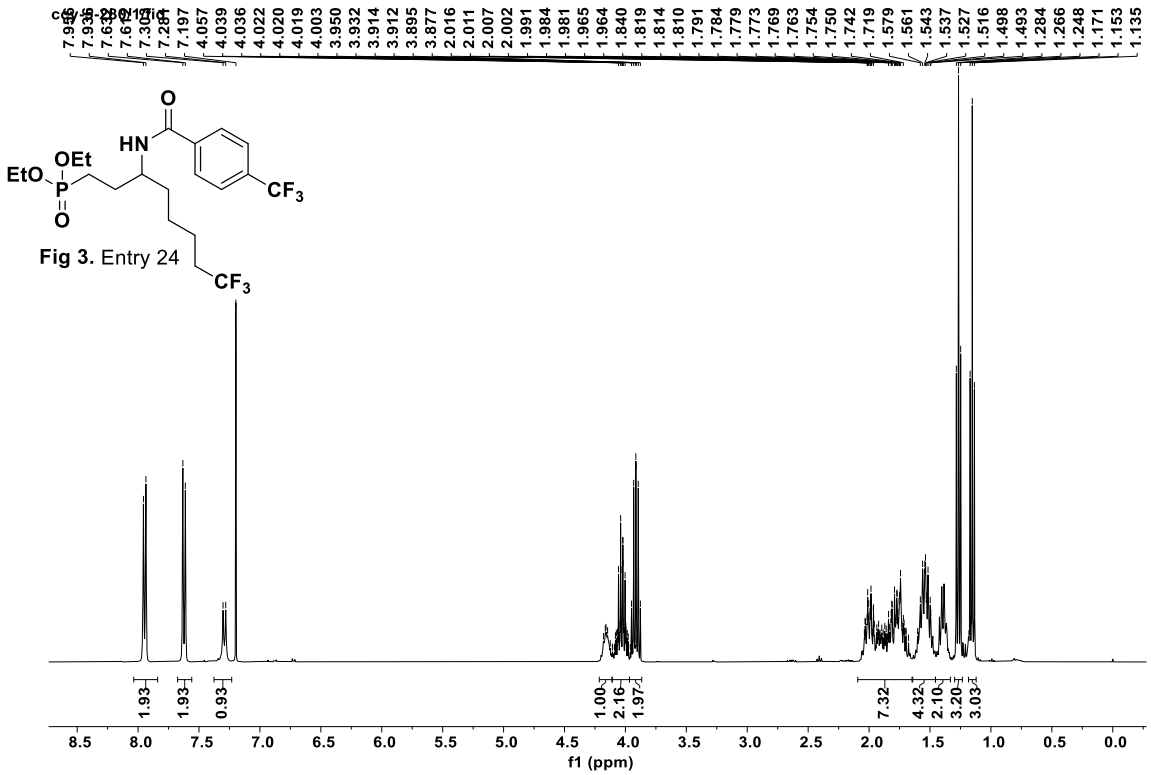

Fig 3. Entry 24

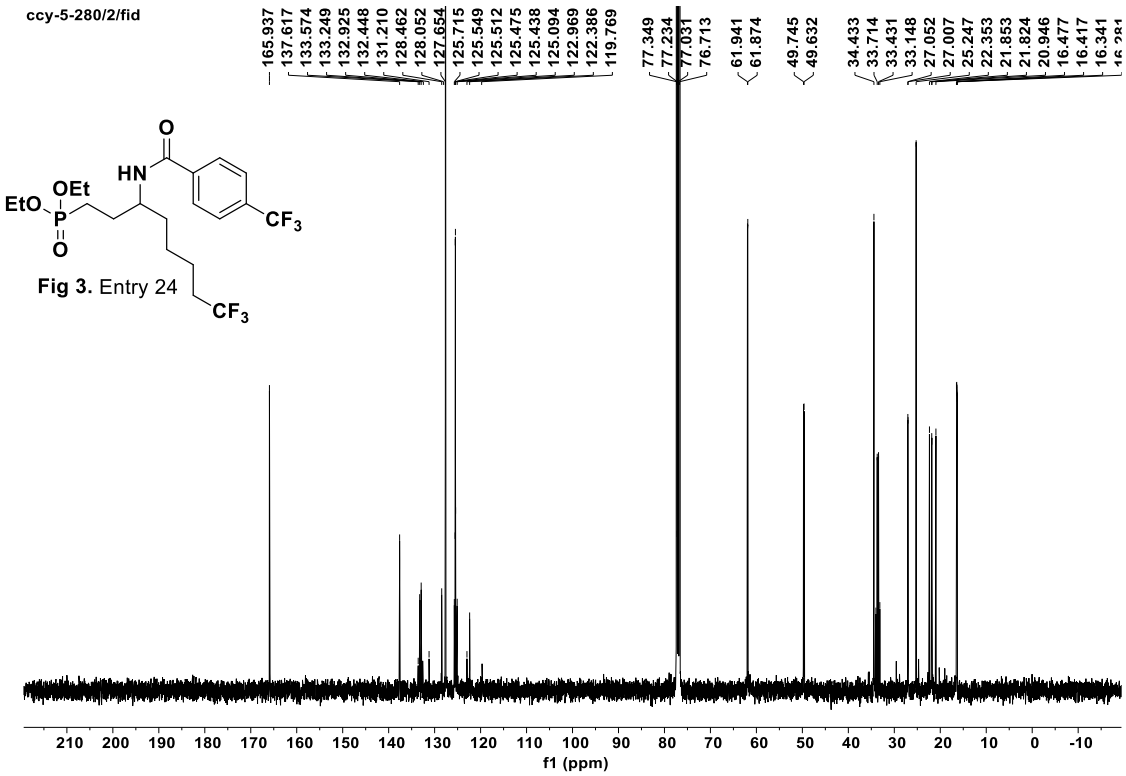

Fig 3. Entry 24

ccy-5-280/3/fid

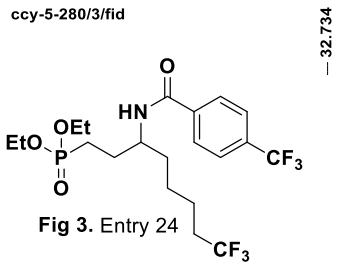

Fig 3. Entry 24

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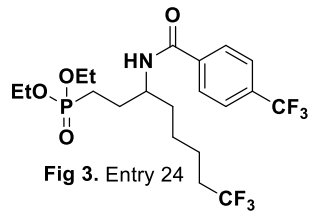

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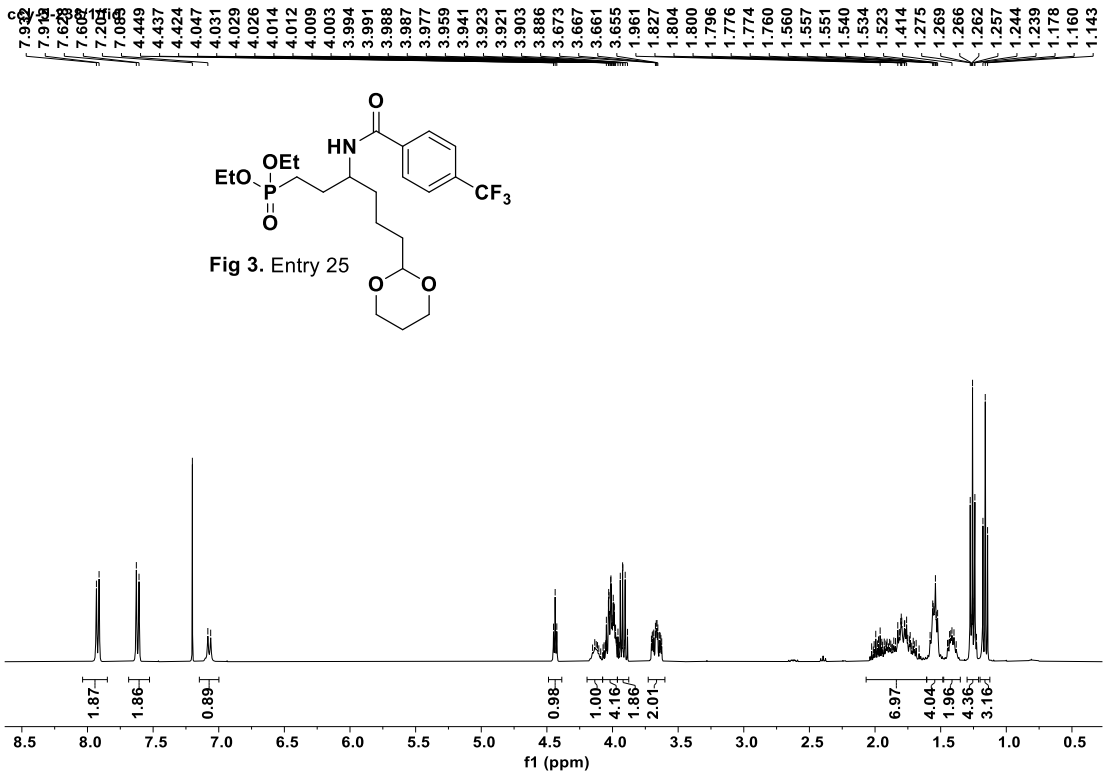
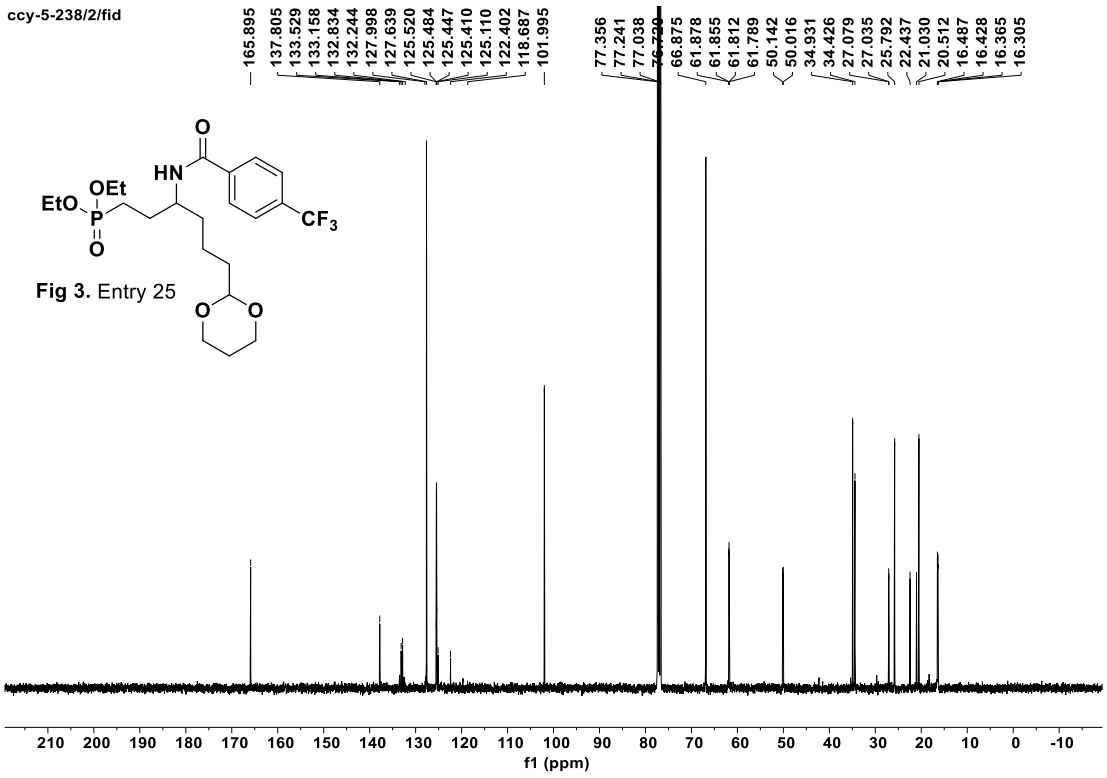


Fig 3. Entry 25
f1 (ppm)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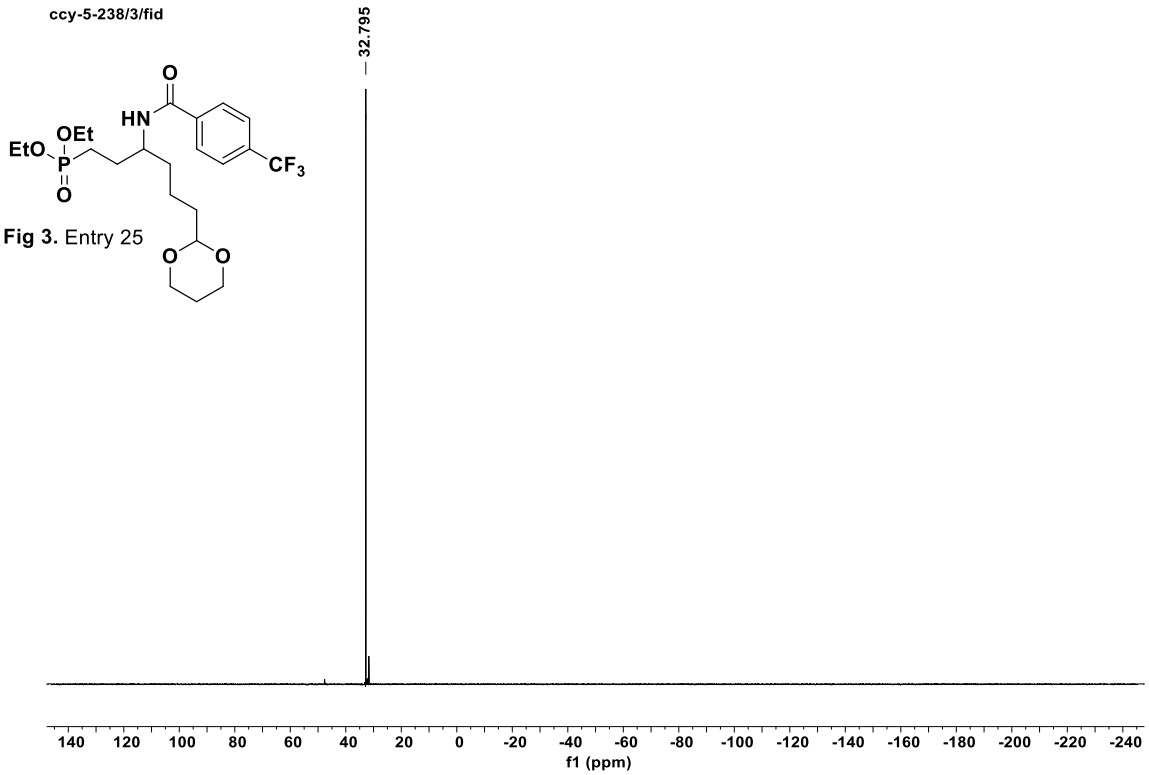
f1 (ppm)



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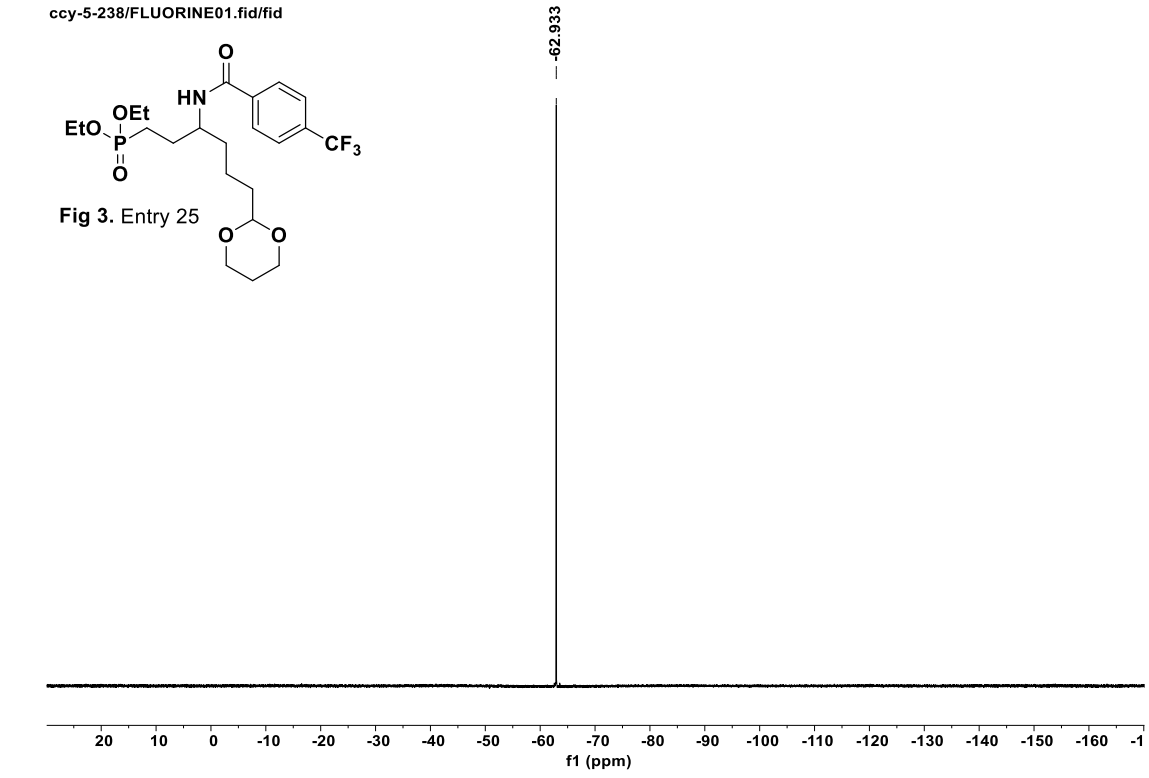
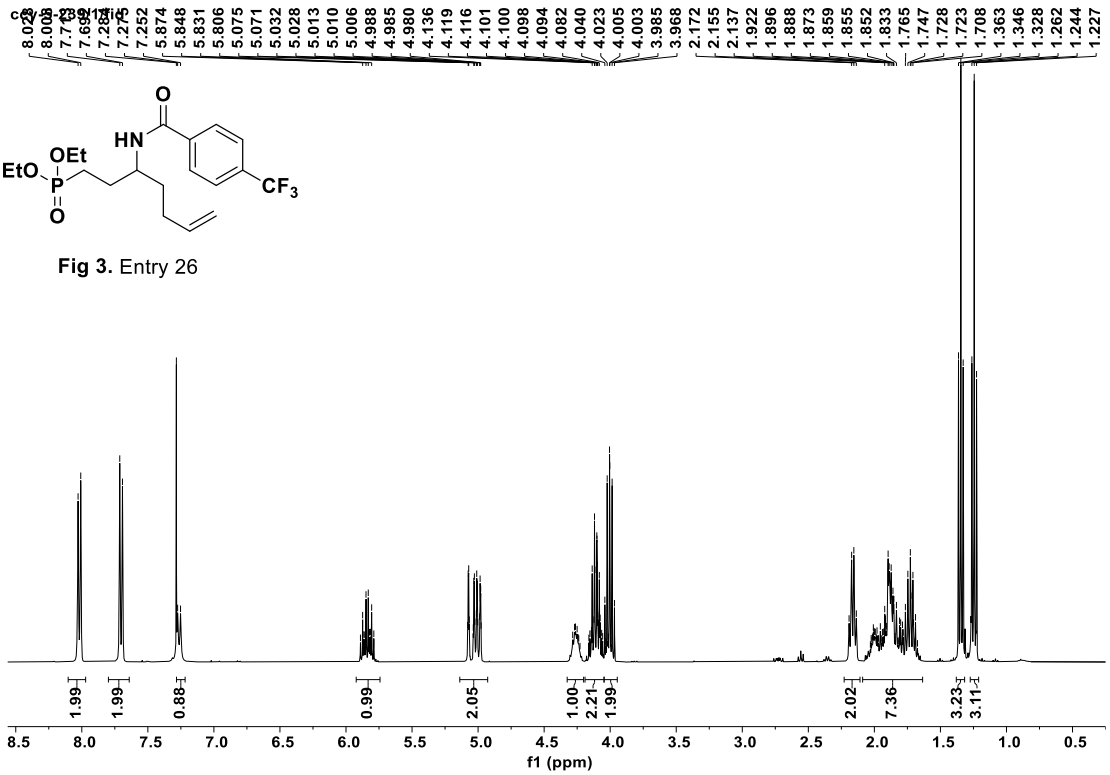


Fig 3. Entry 25



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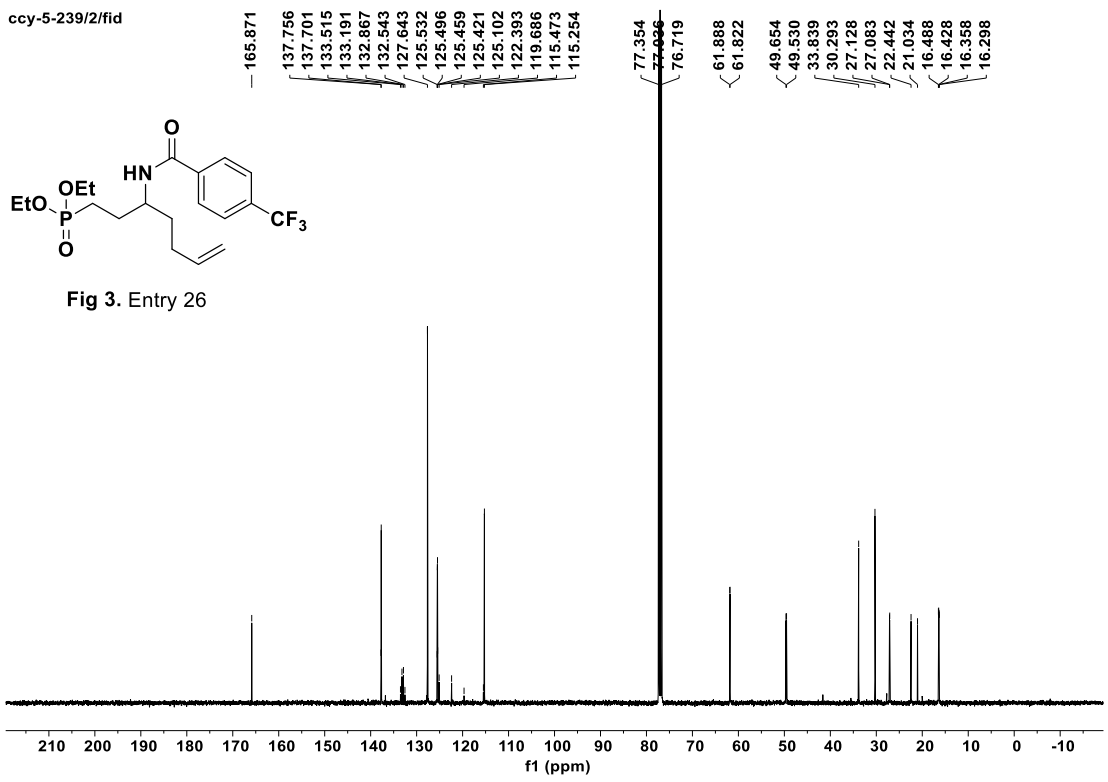

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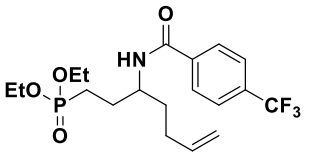

Fig 3. Entry 26

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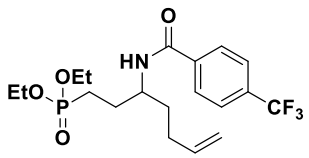

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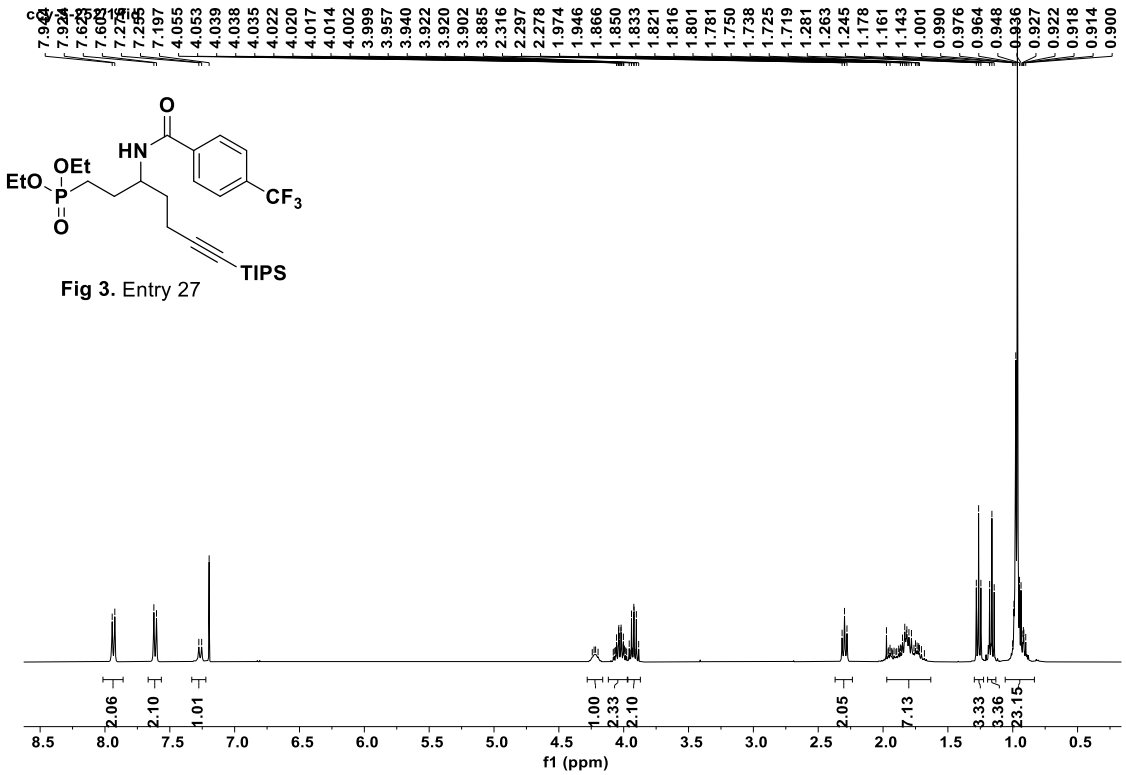

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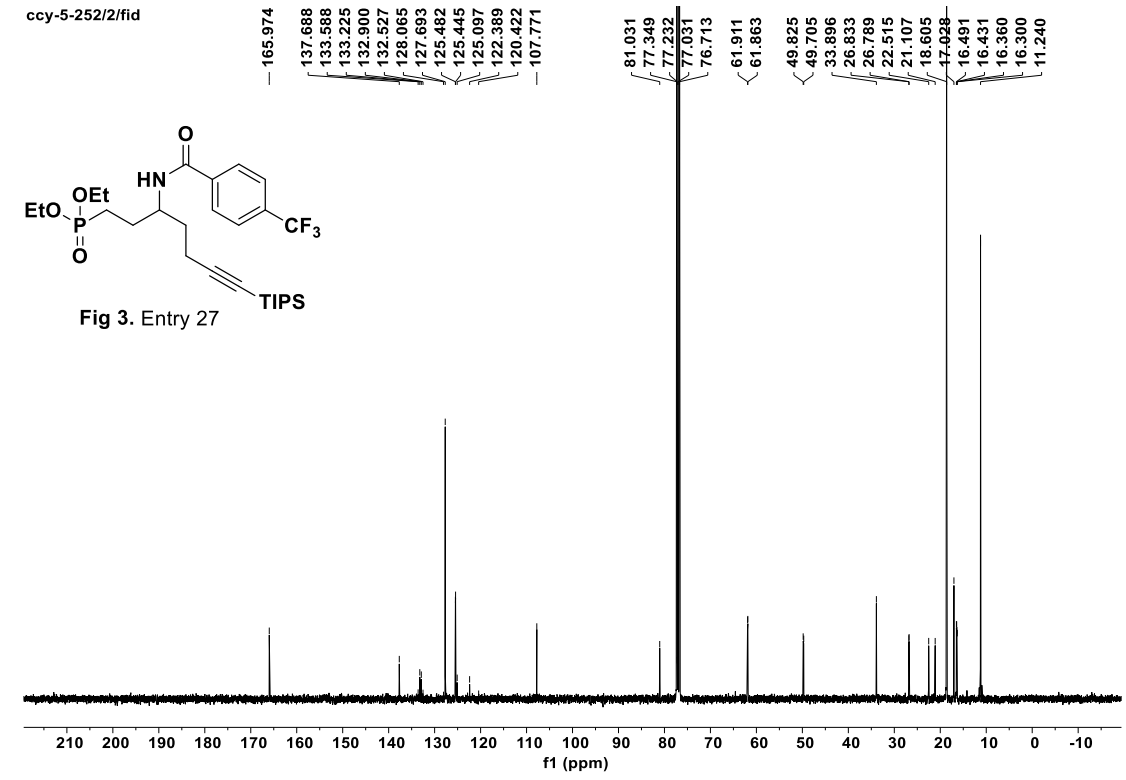

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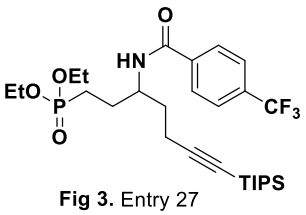

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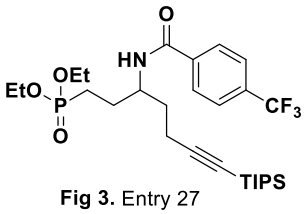

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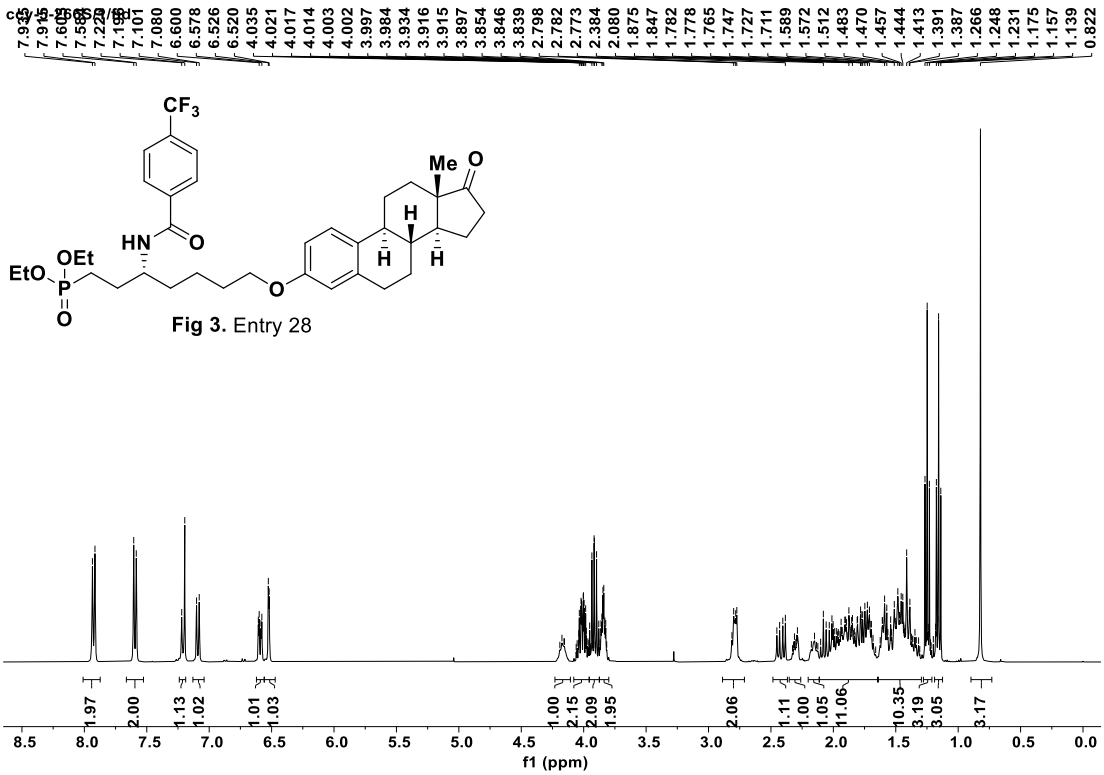

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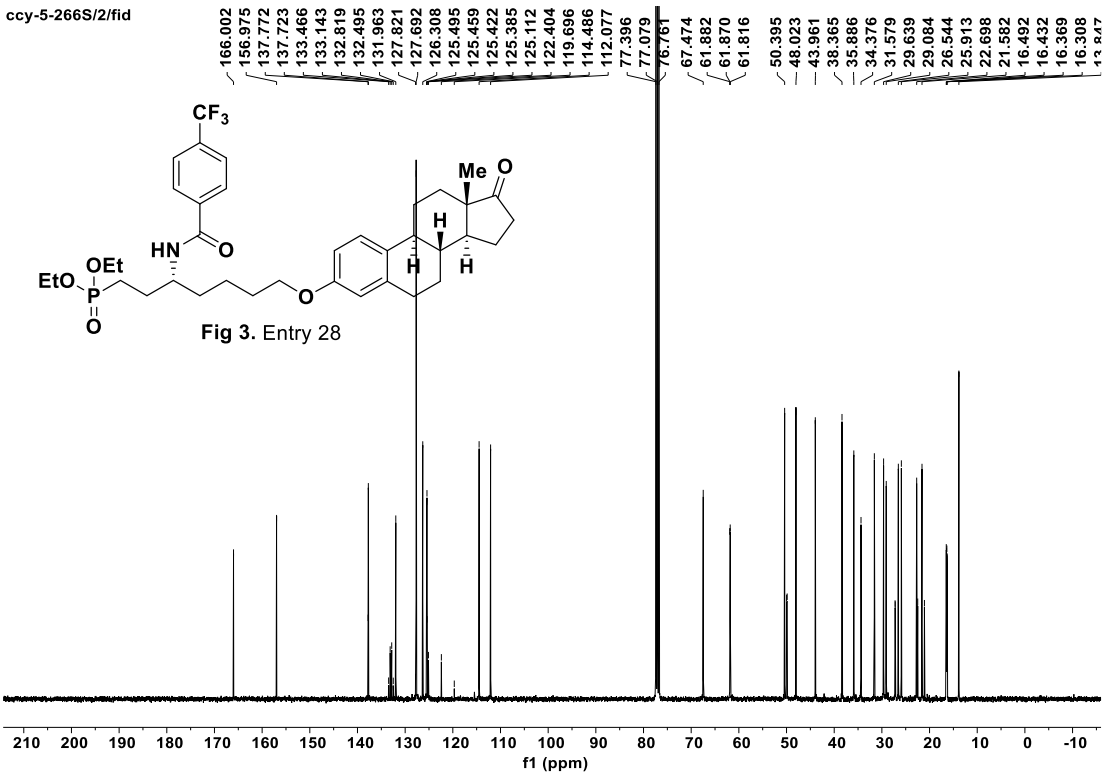

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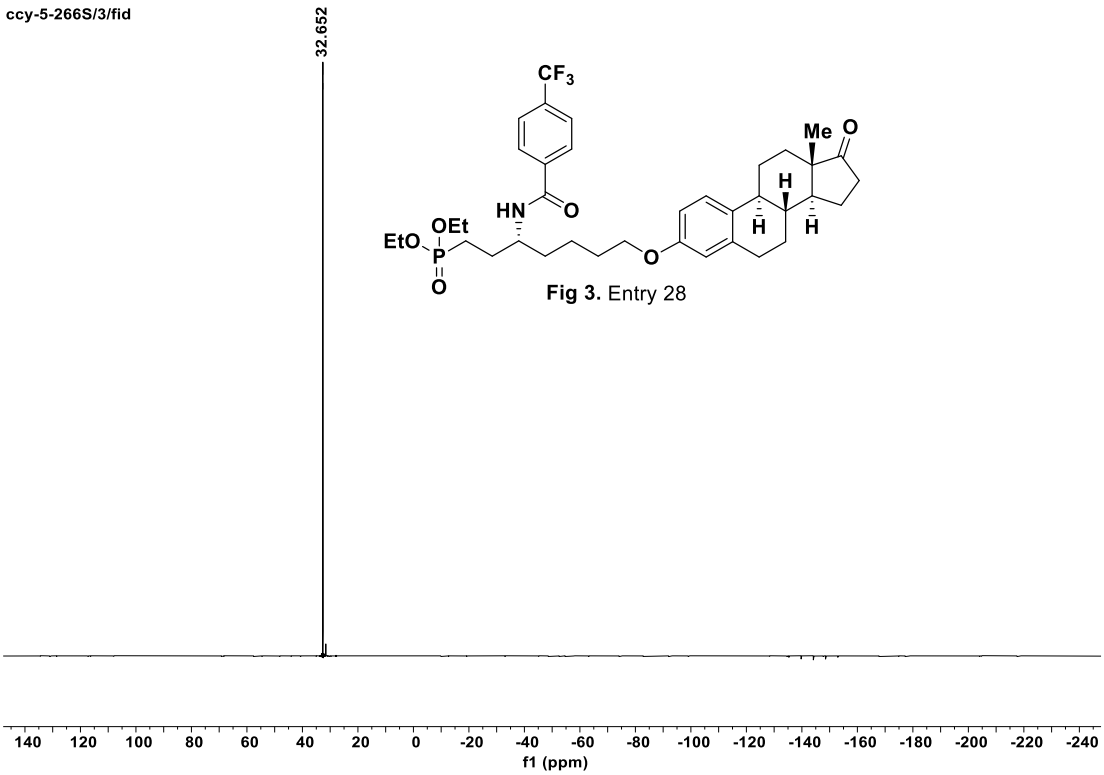

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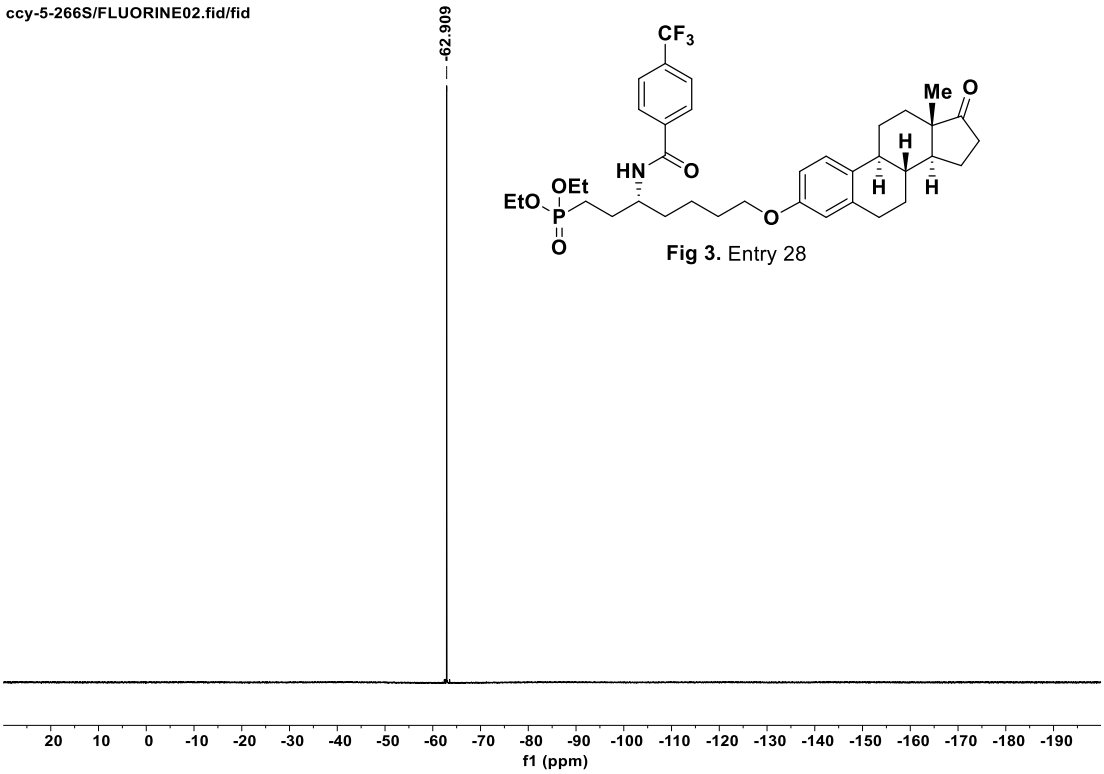

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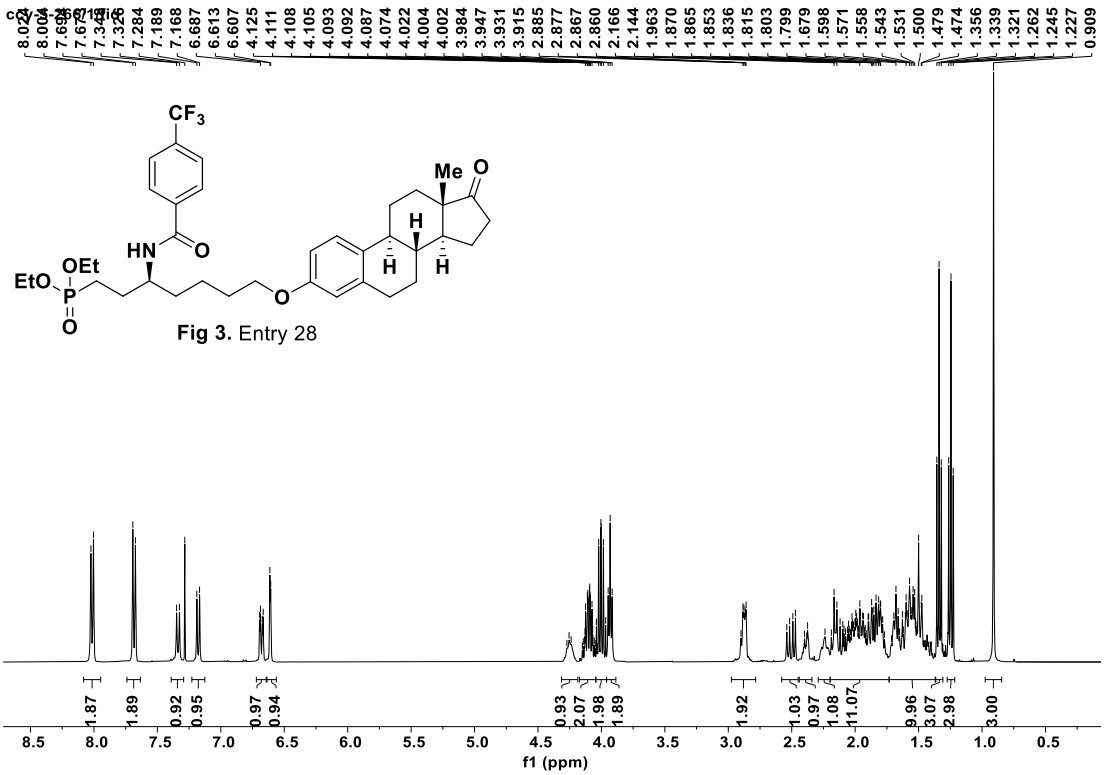

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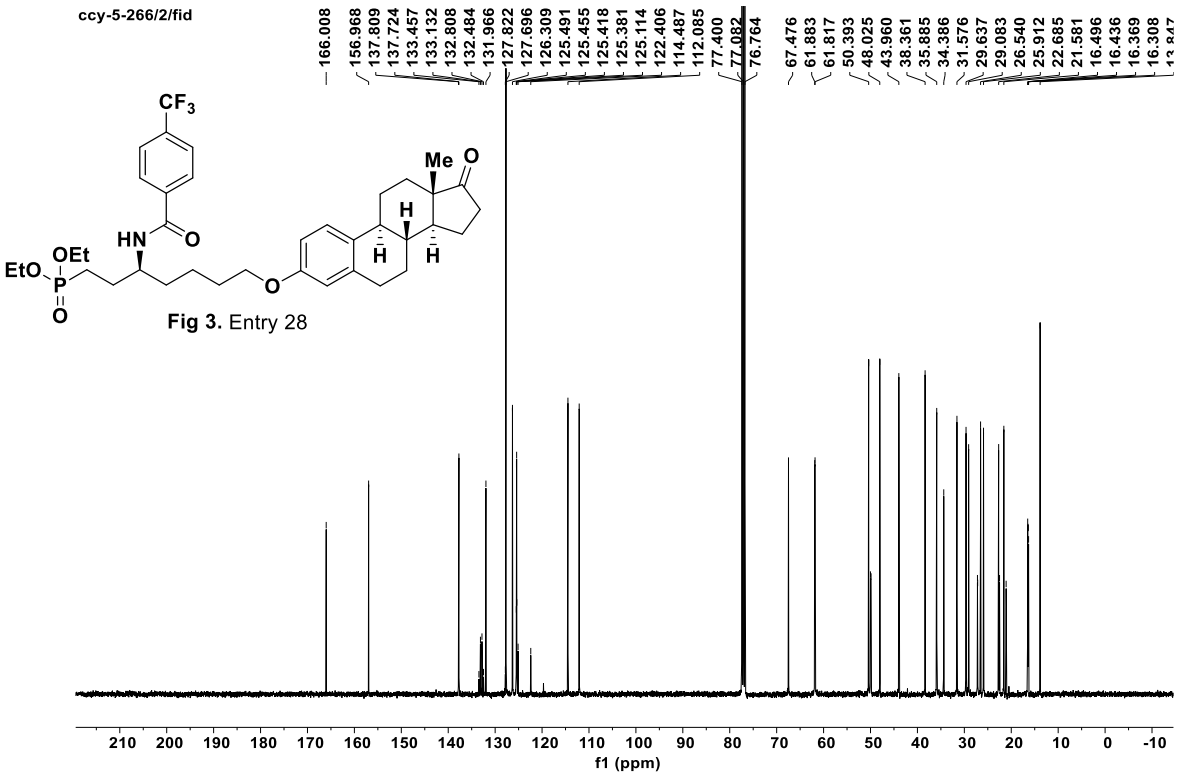

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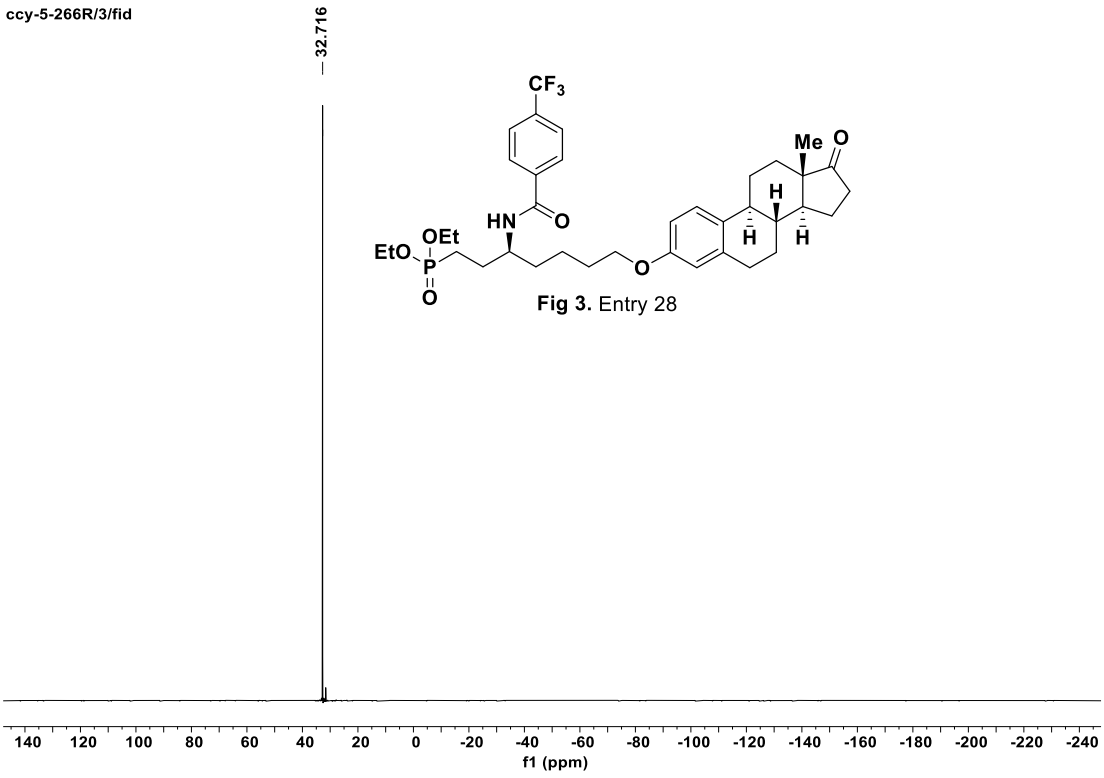

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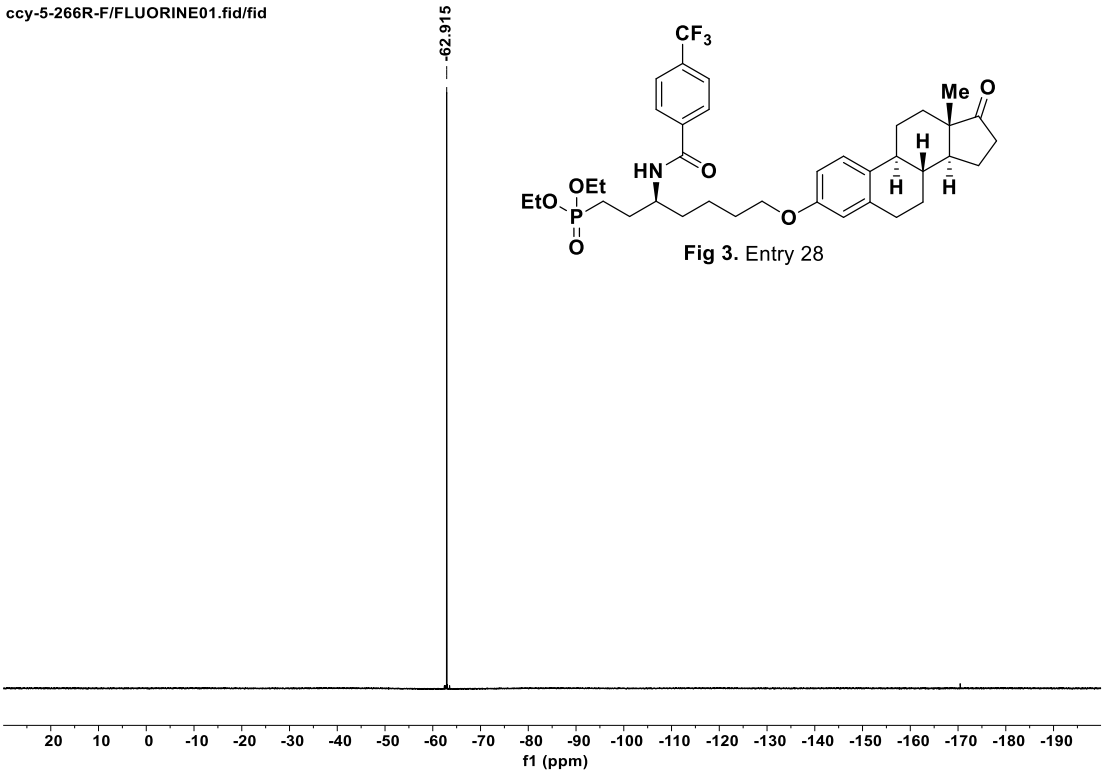

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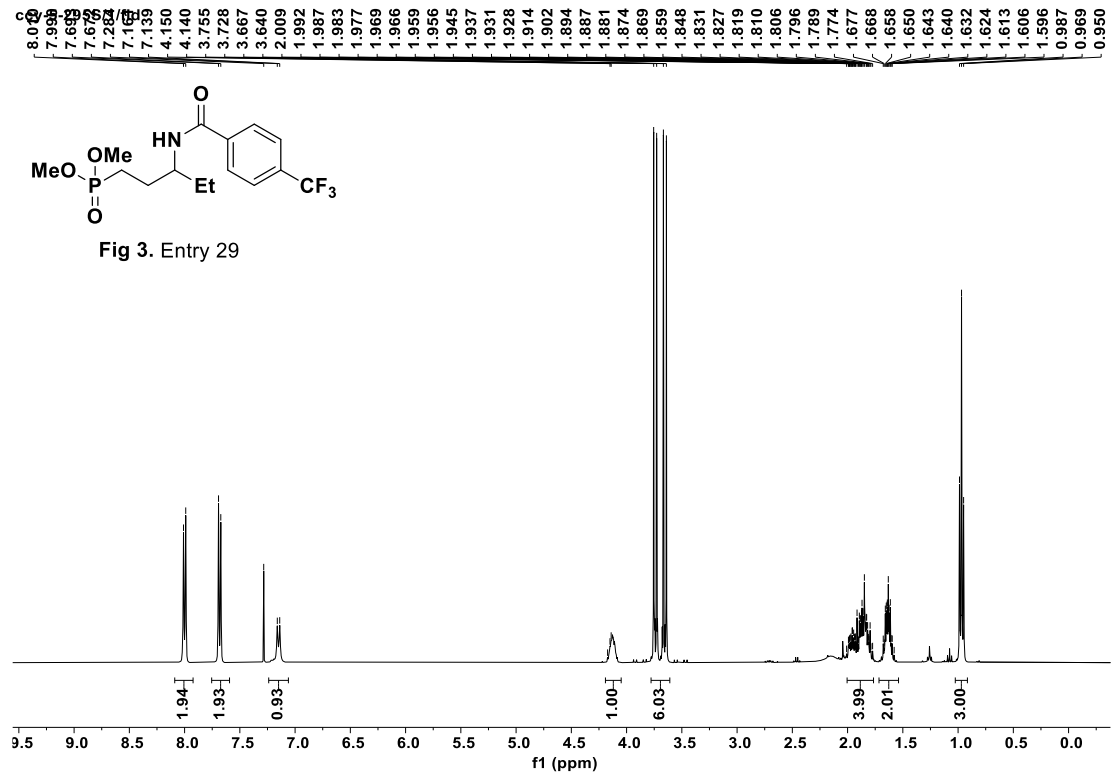

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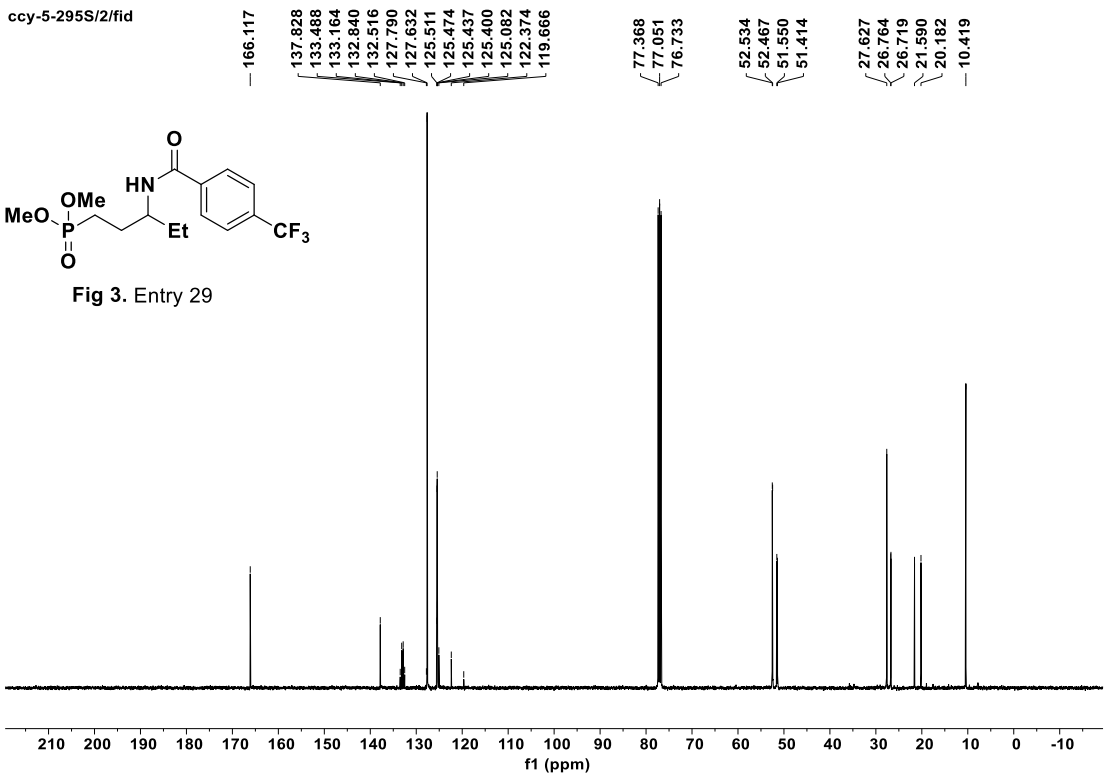

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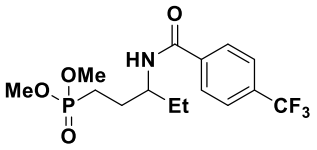

Fig 3. Entry 29

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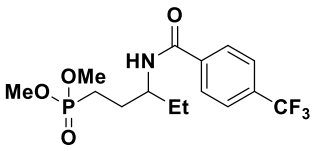

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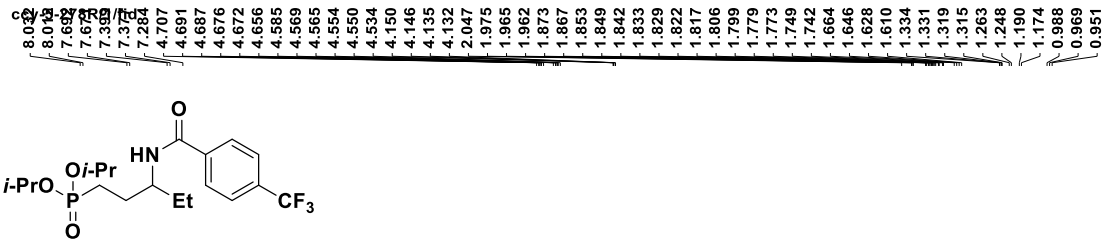

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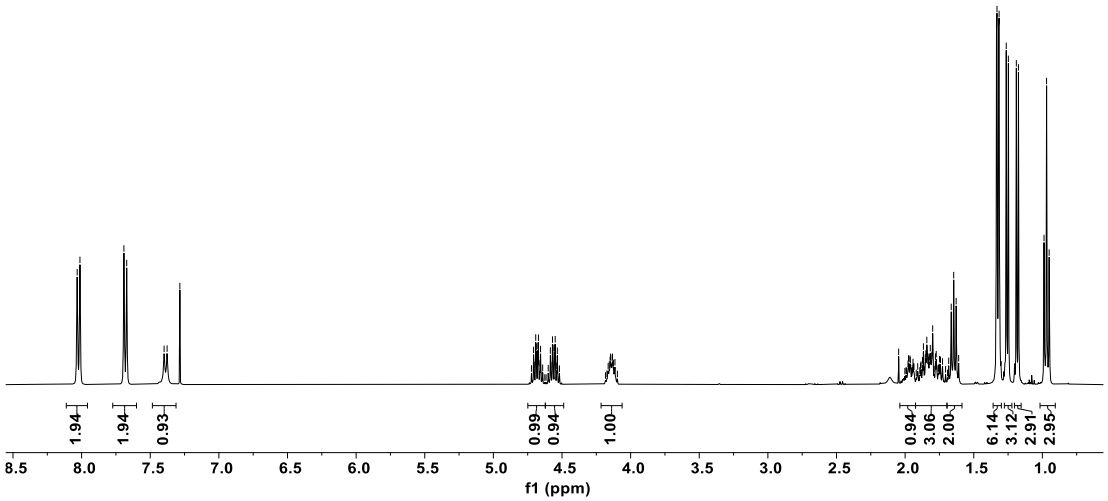

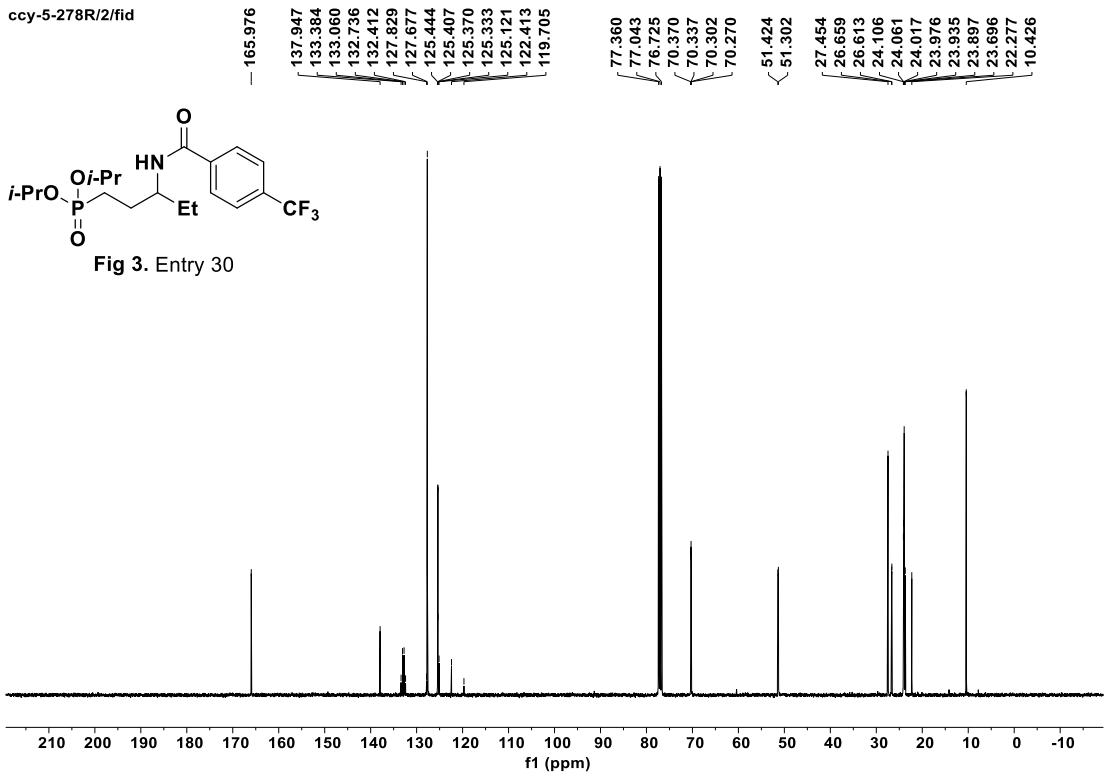

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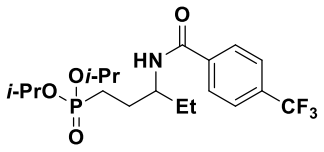

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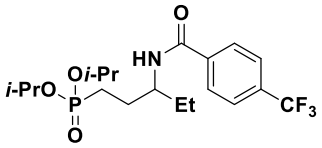

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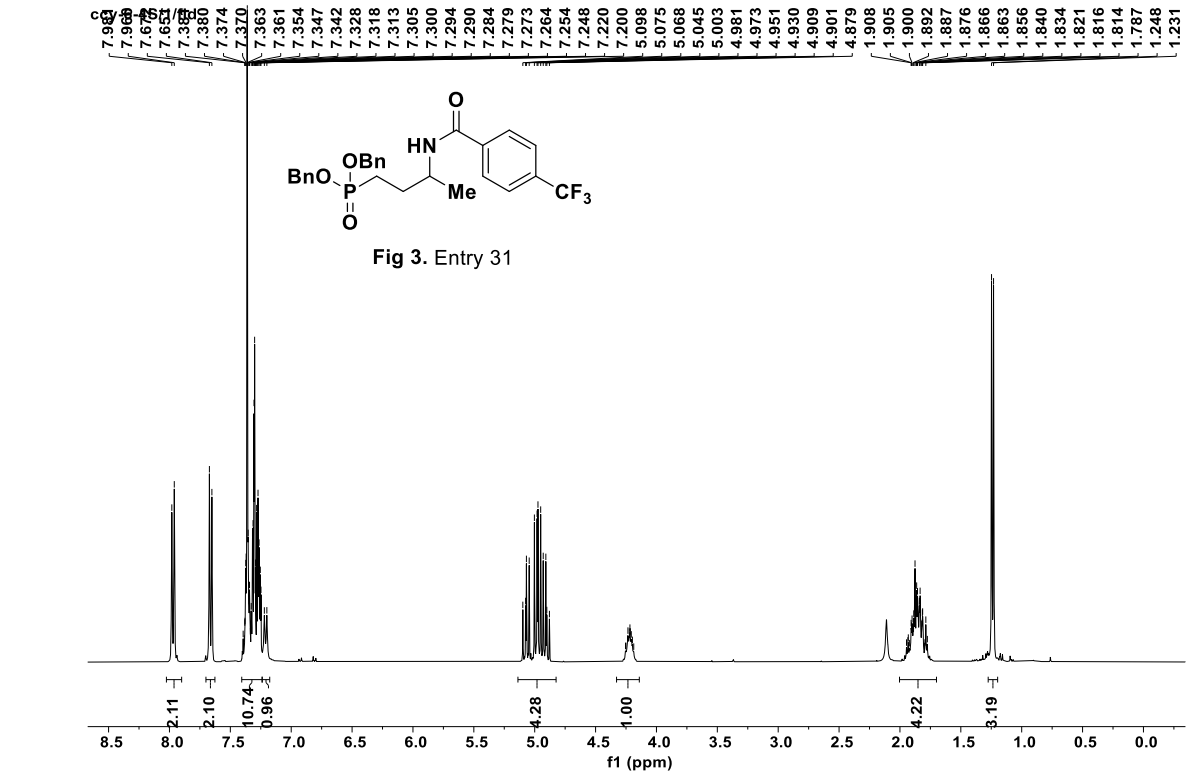

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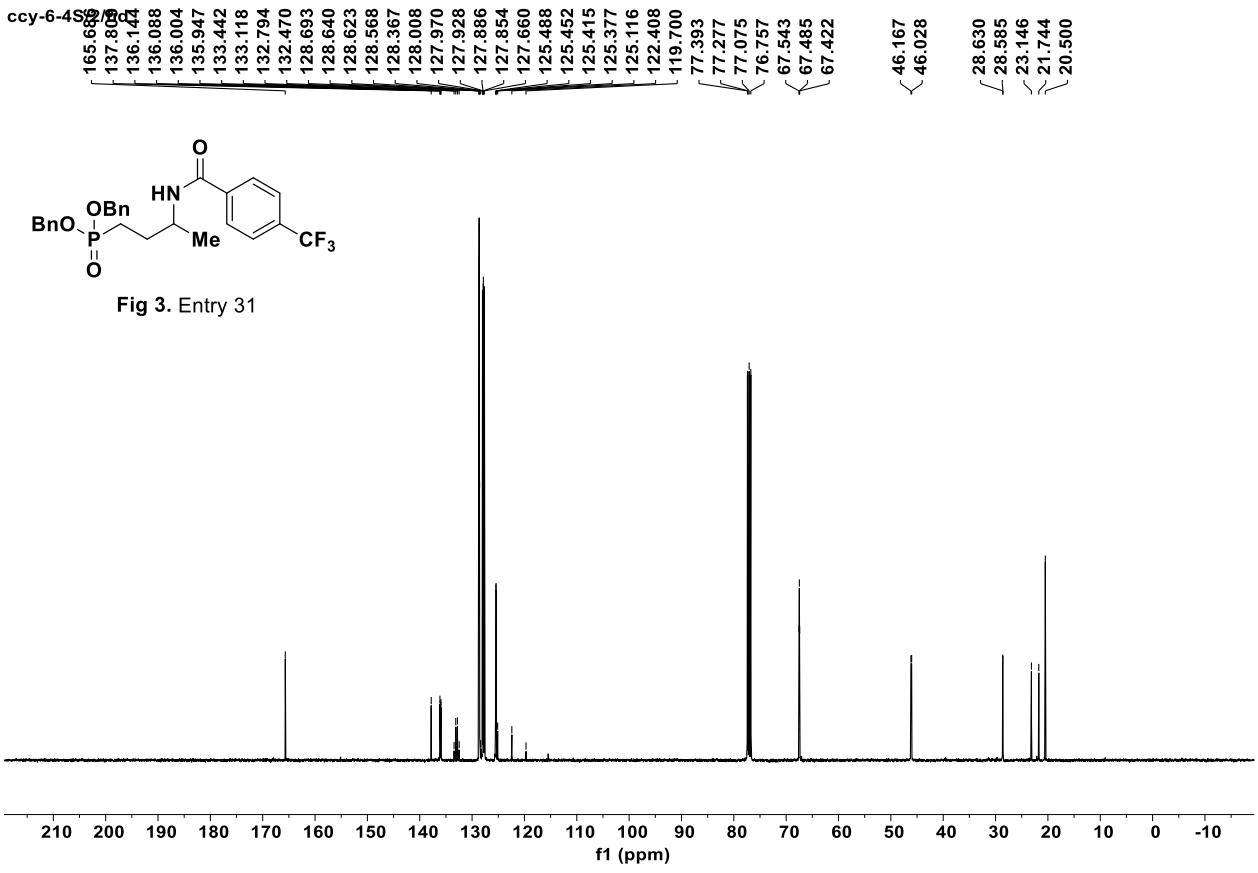

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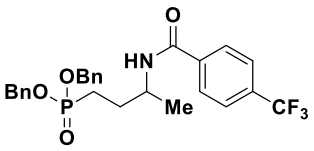

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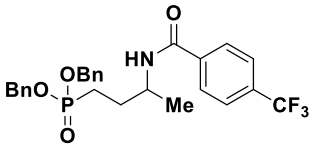

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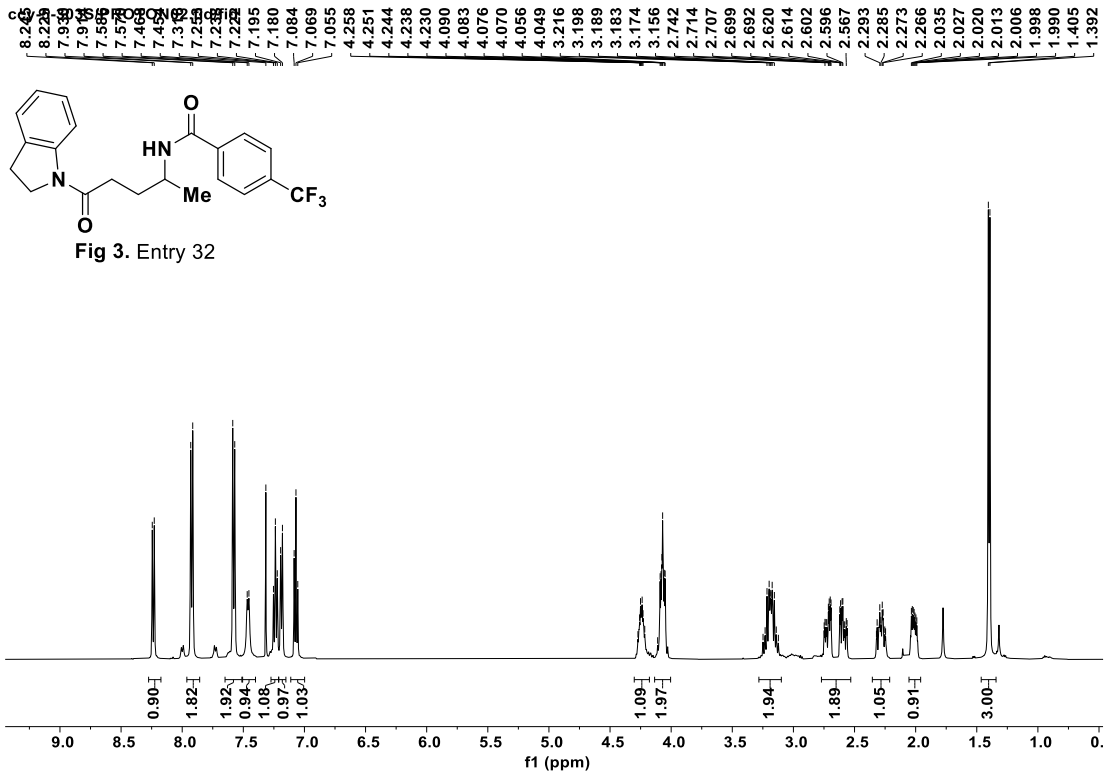

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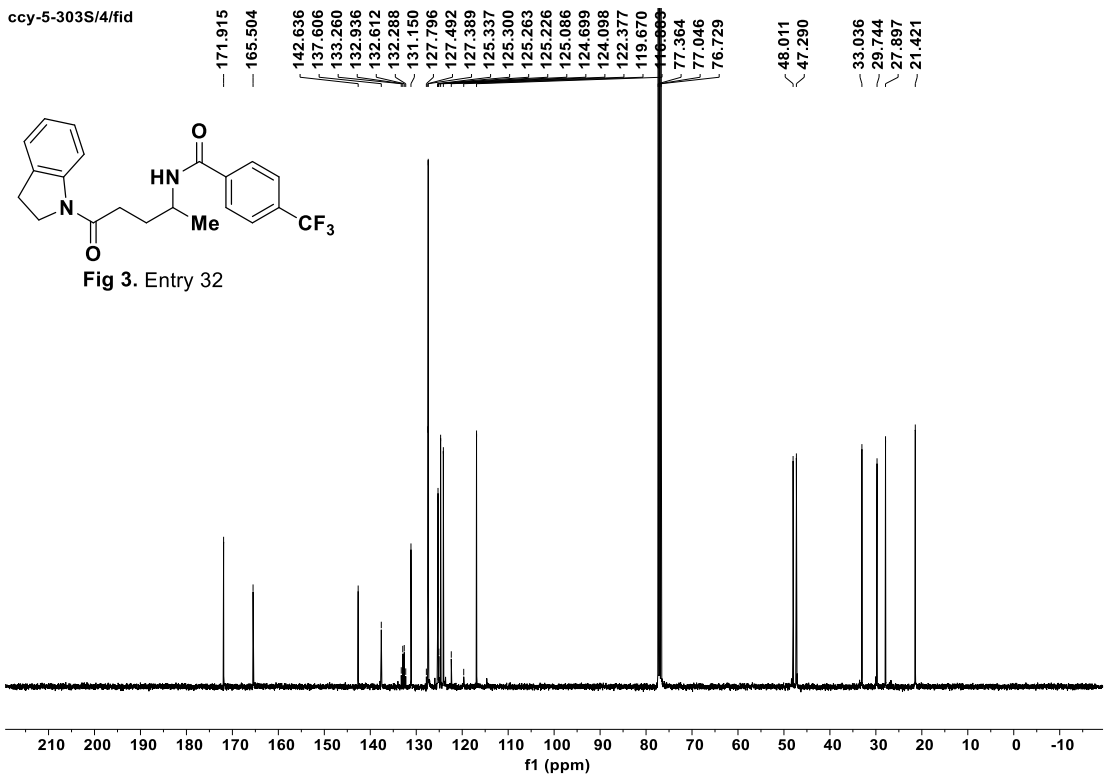

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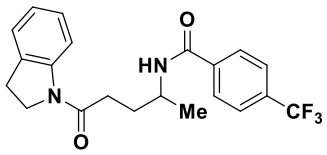

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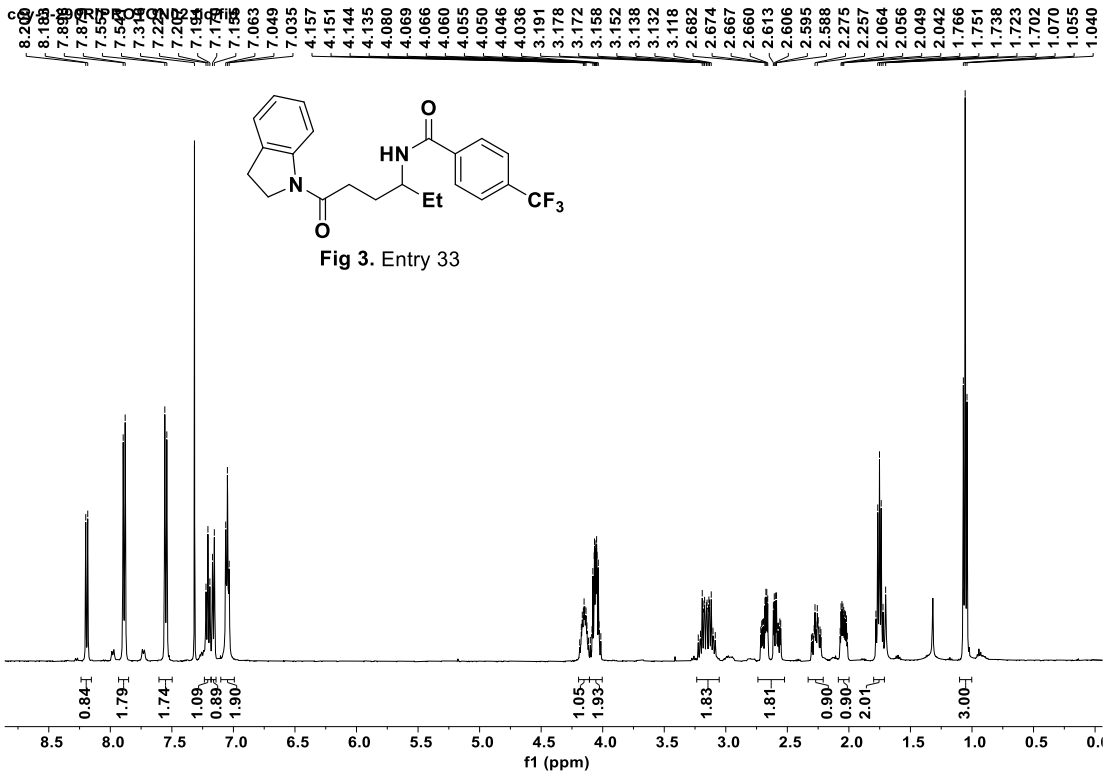

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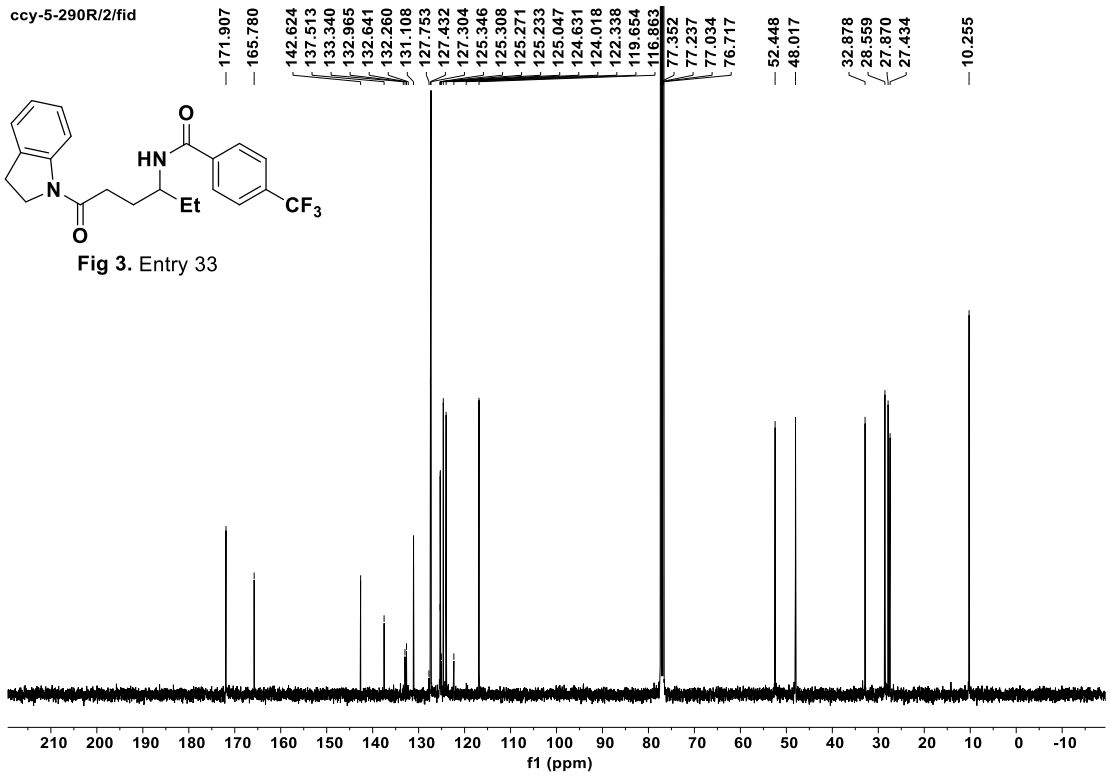

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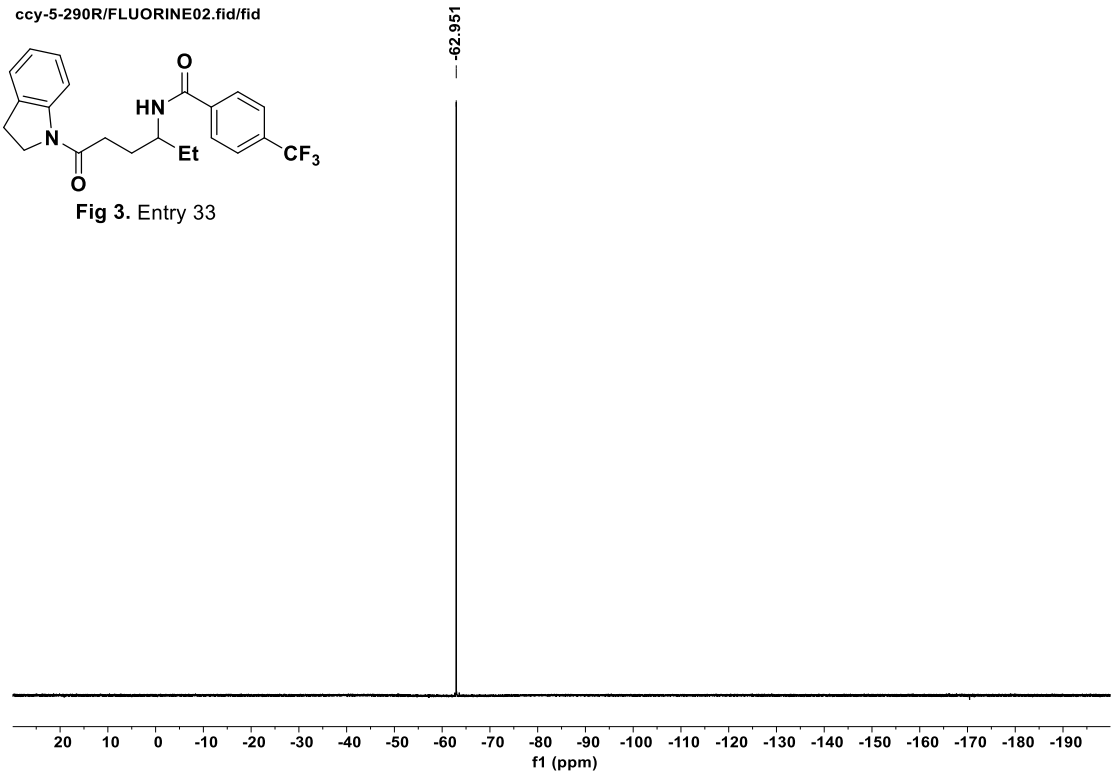

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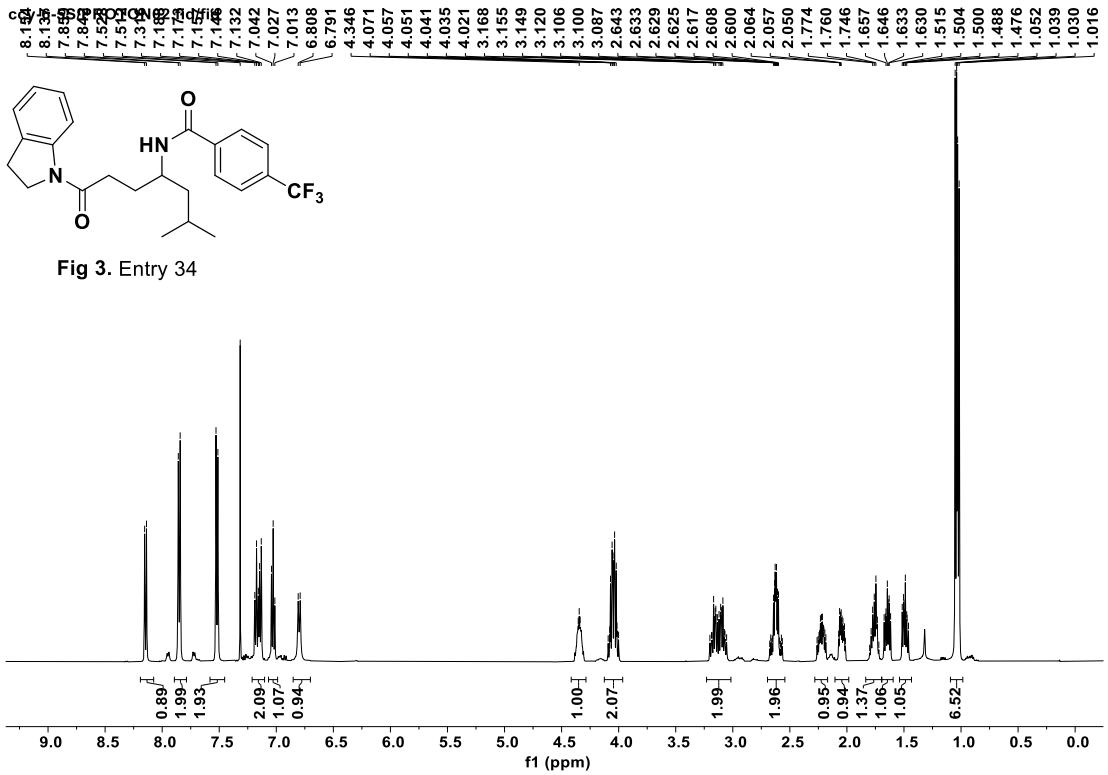

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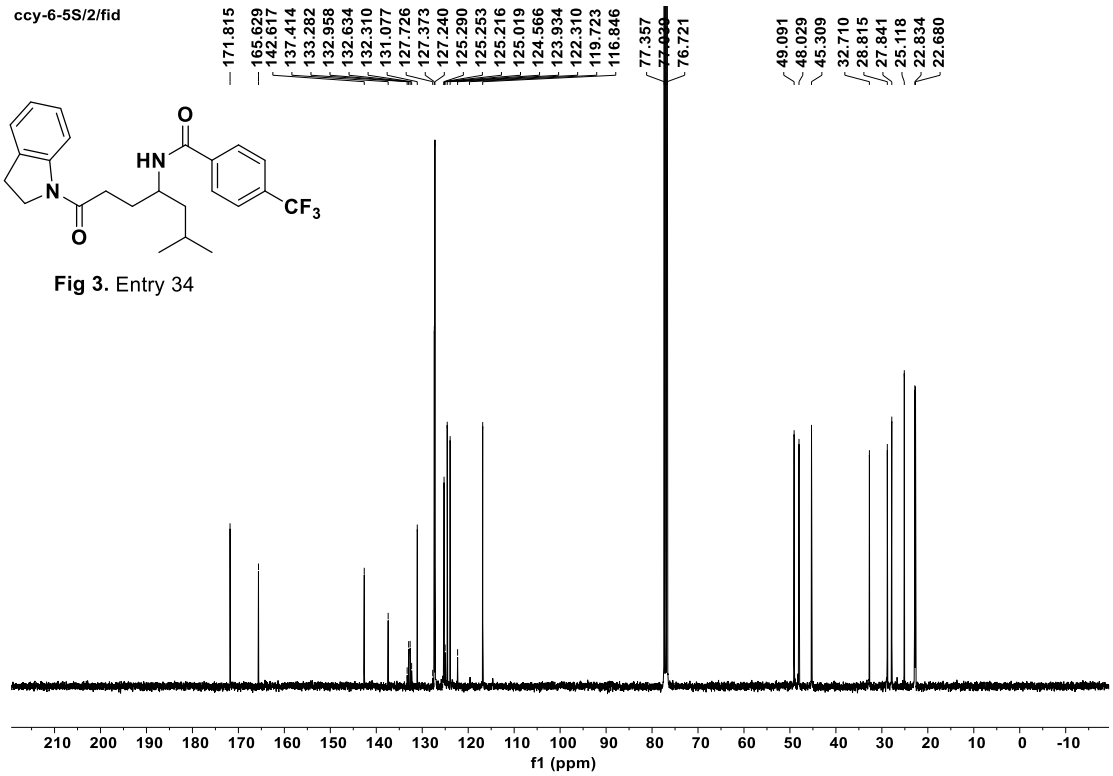

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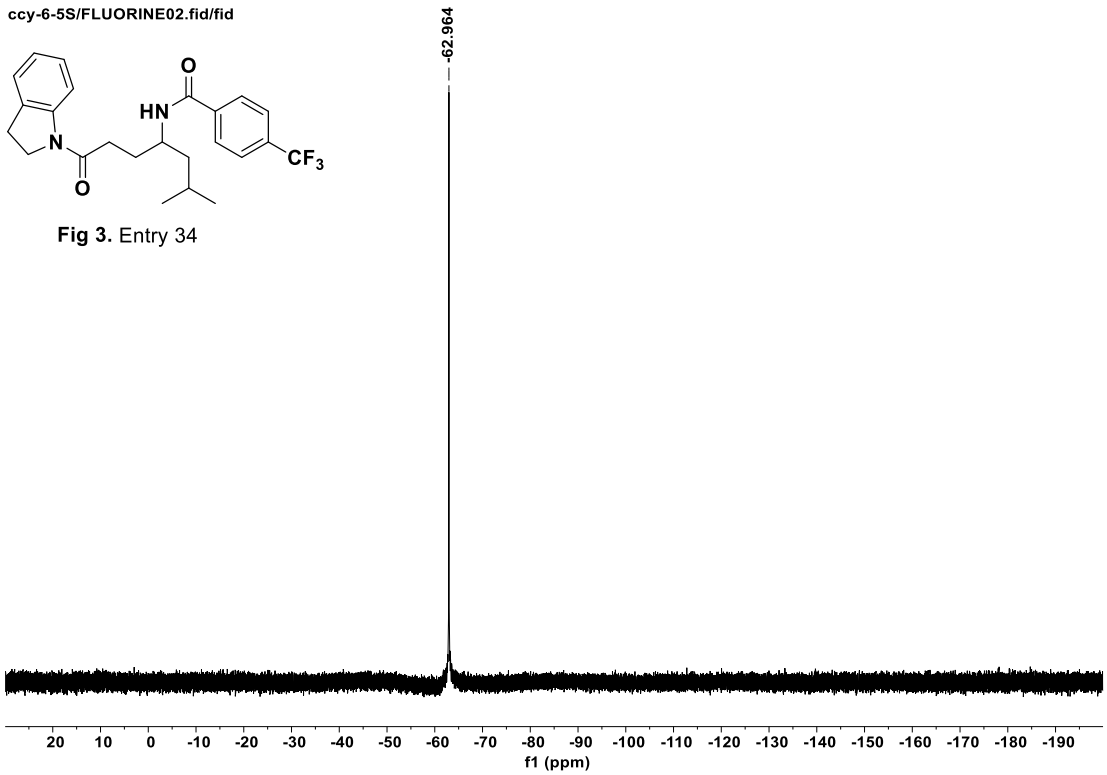

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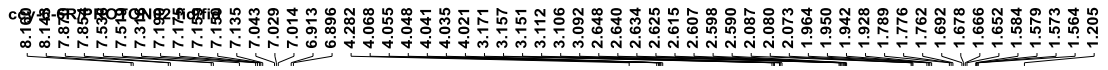

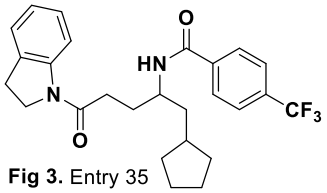

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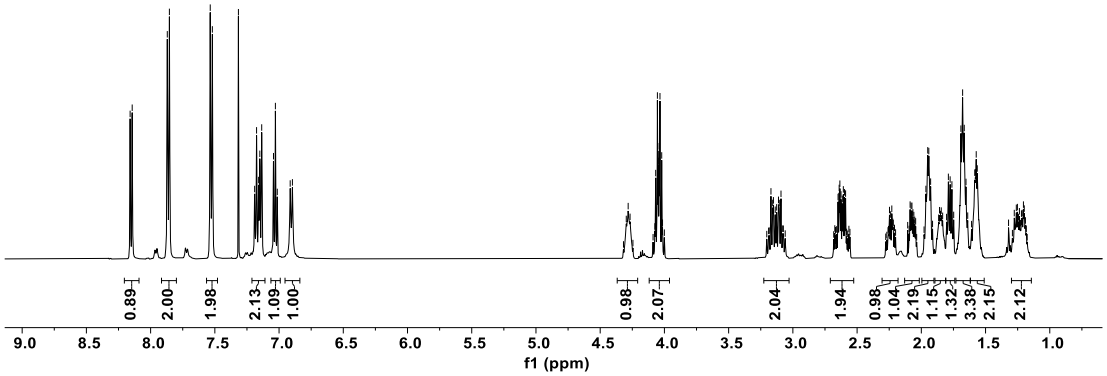

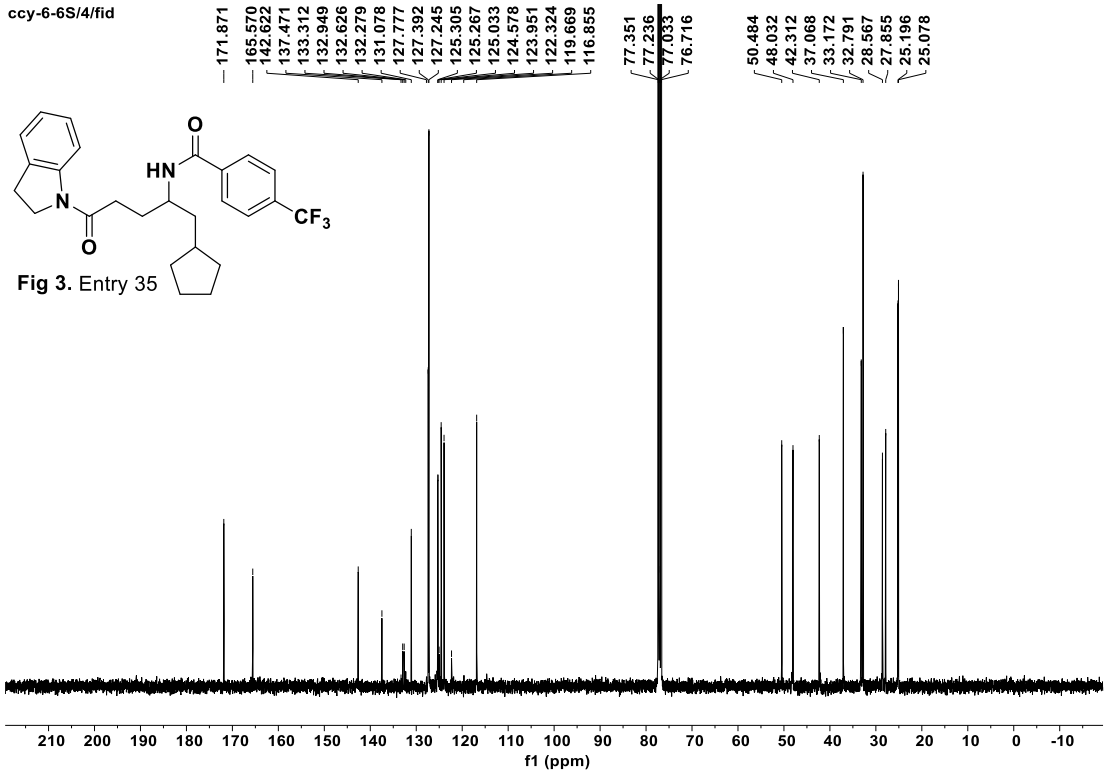

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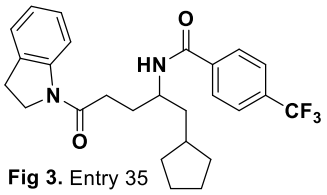

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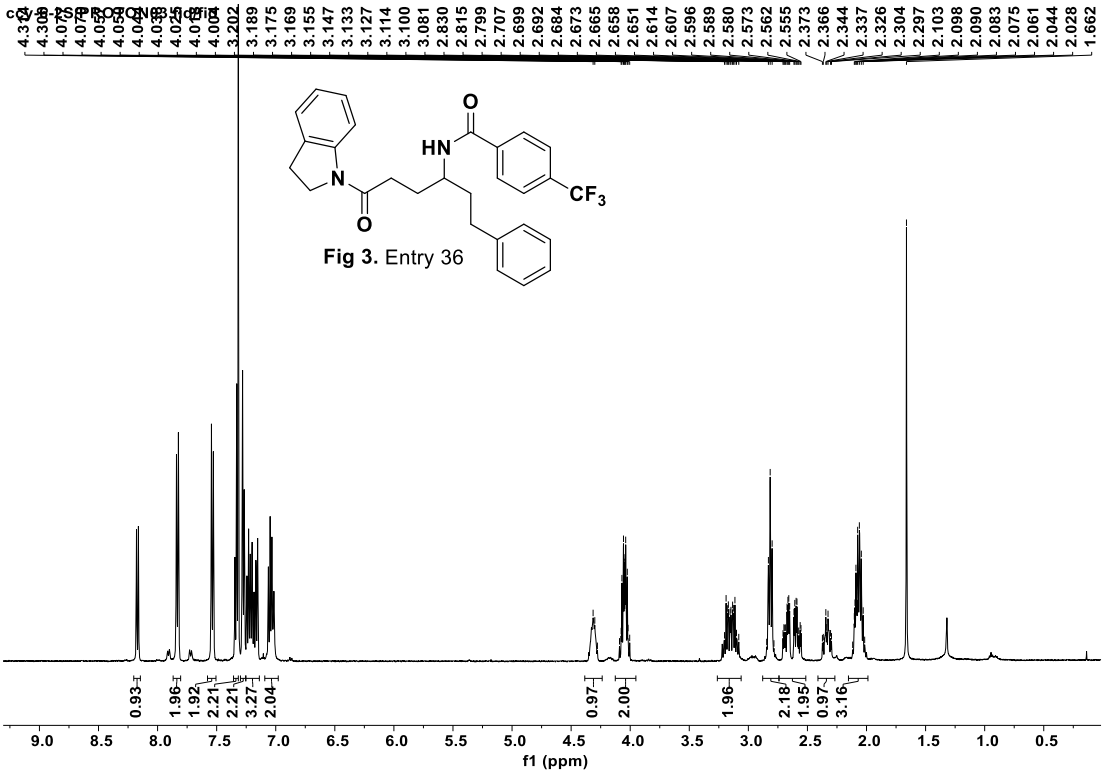

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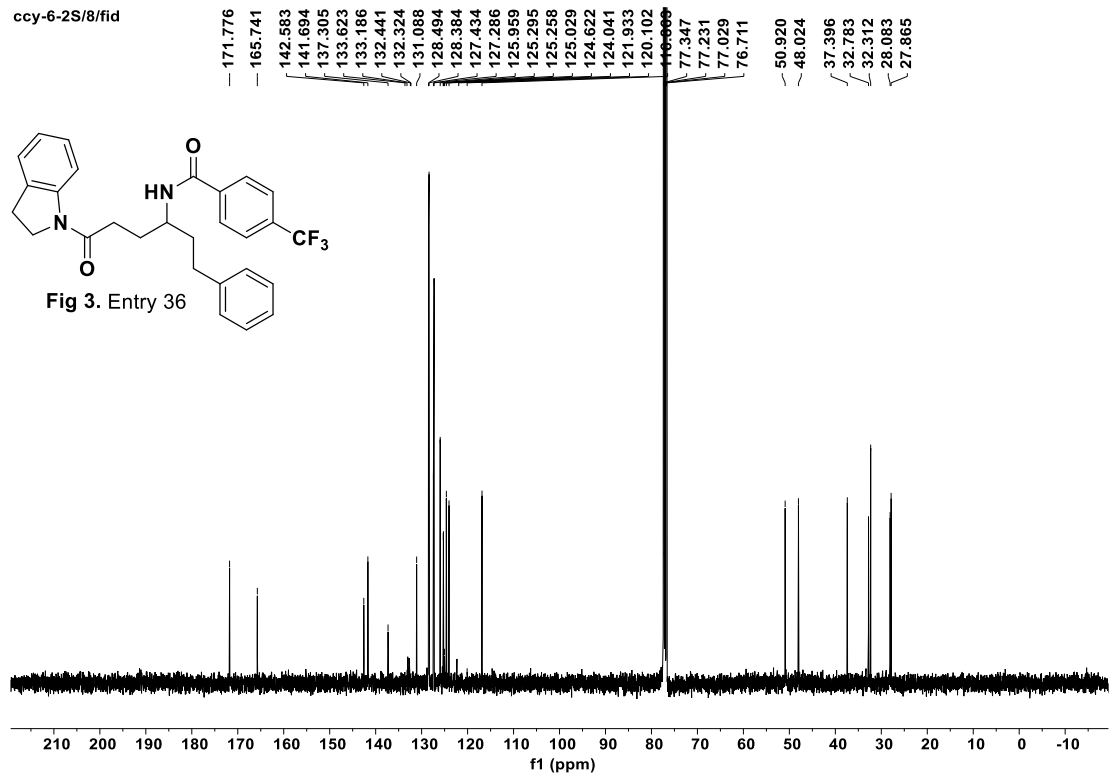

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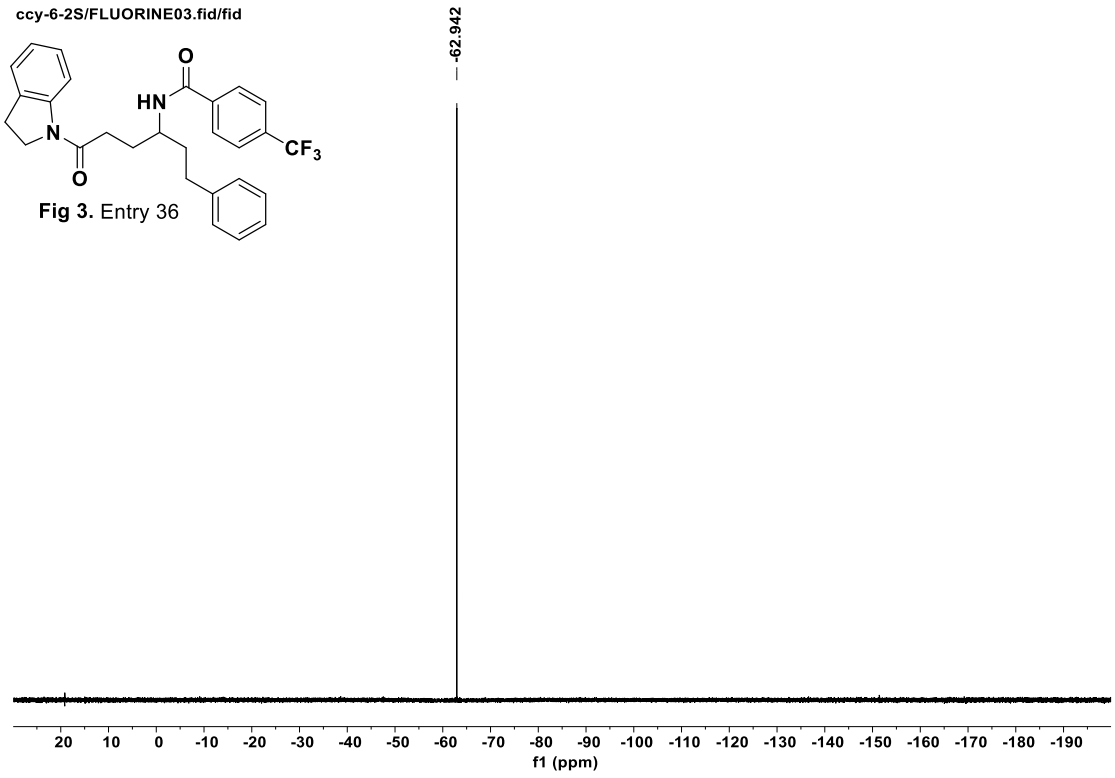

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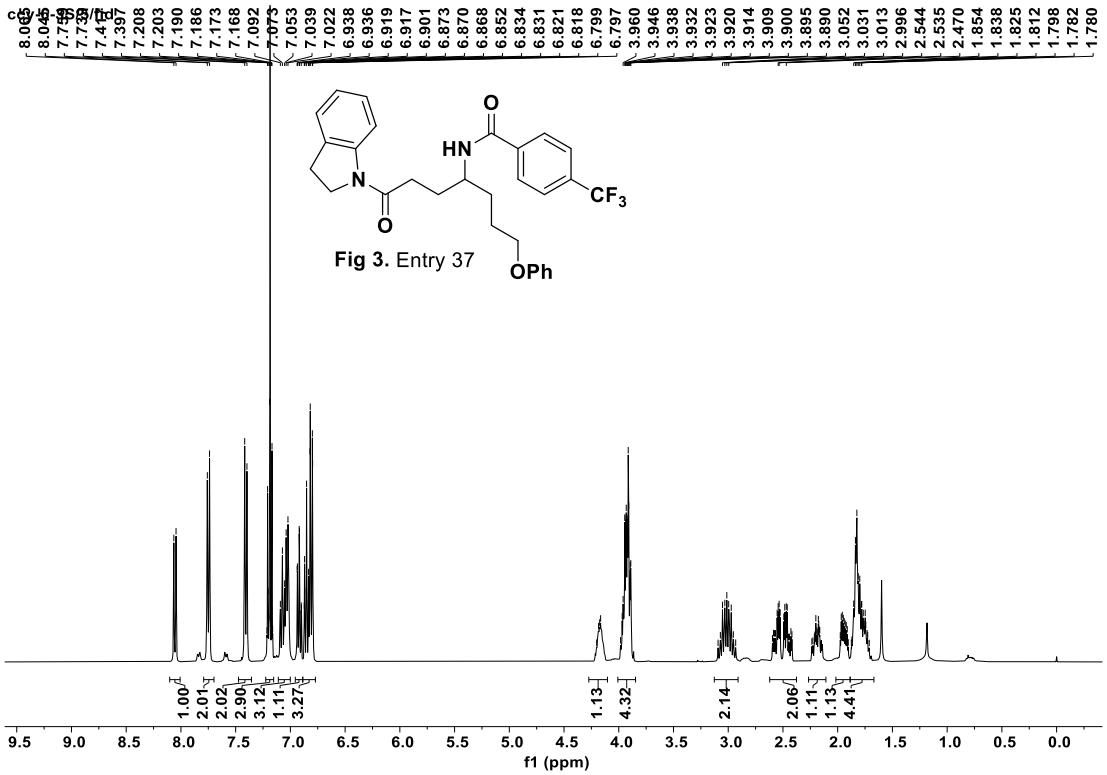

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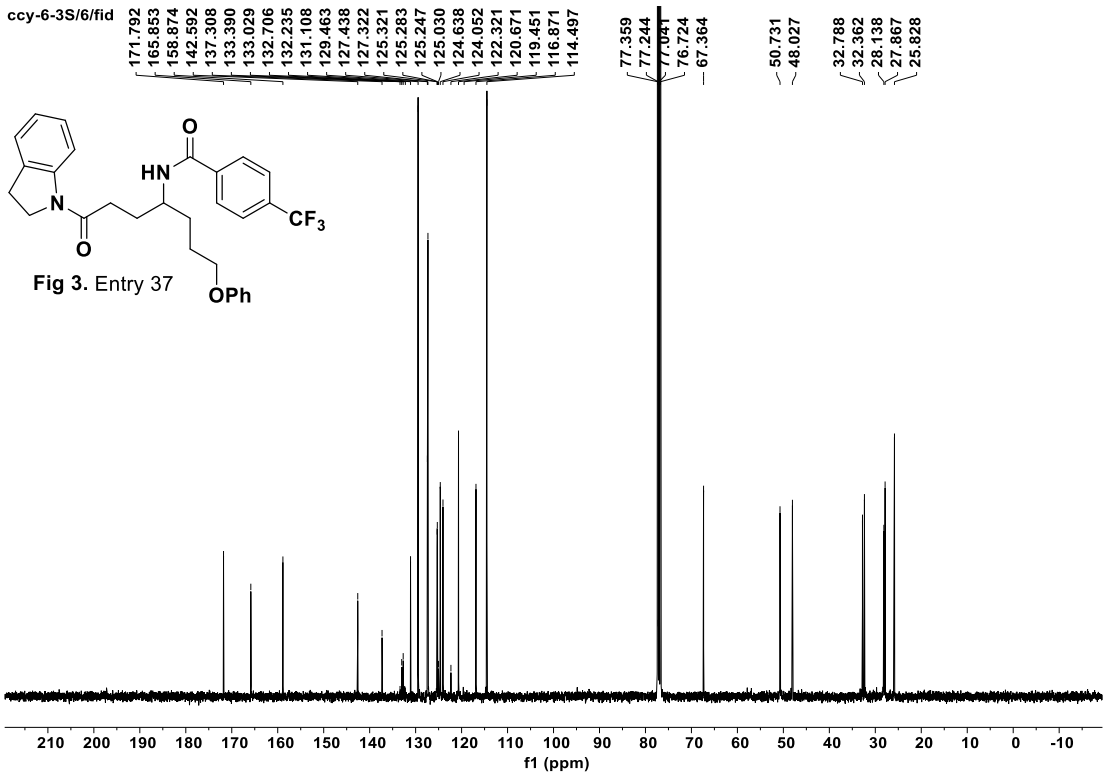

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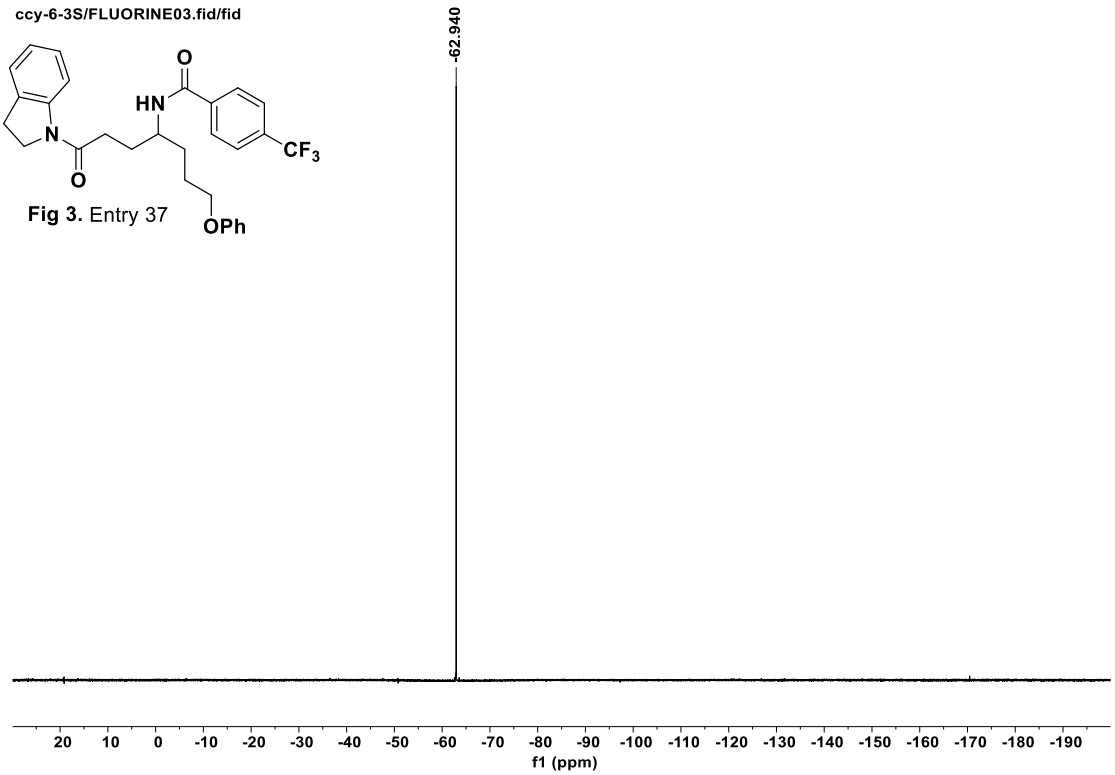

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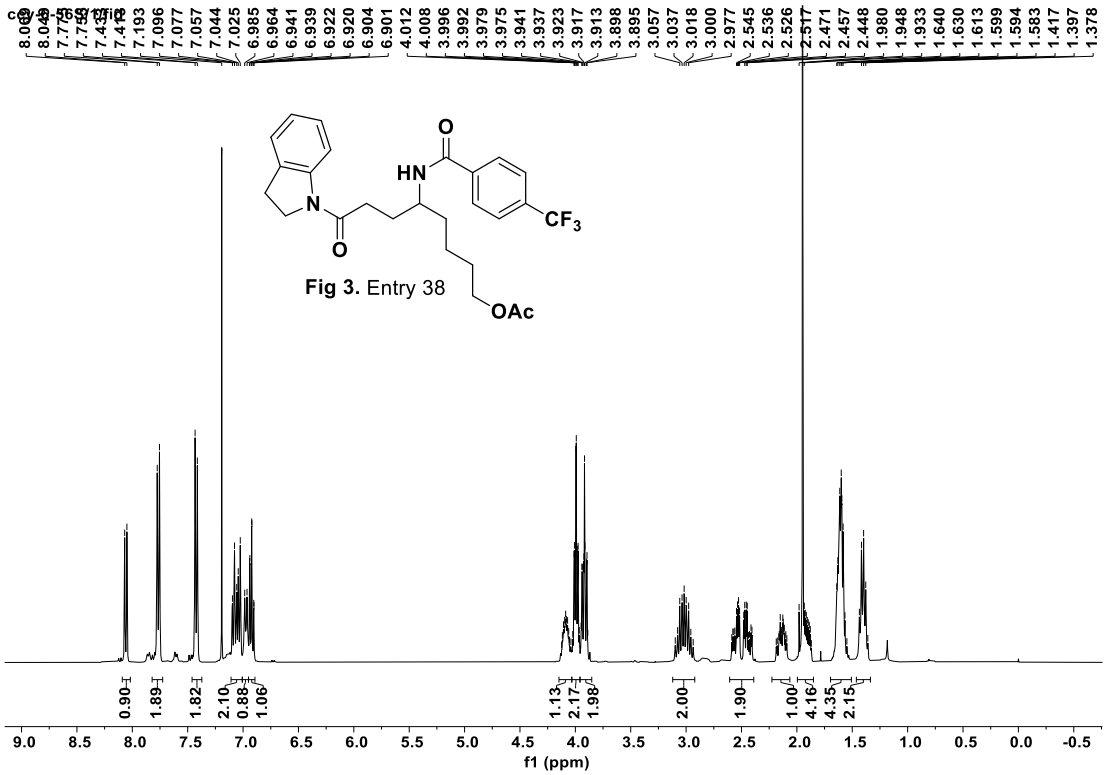

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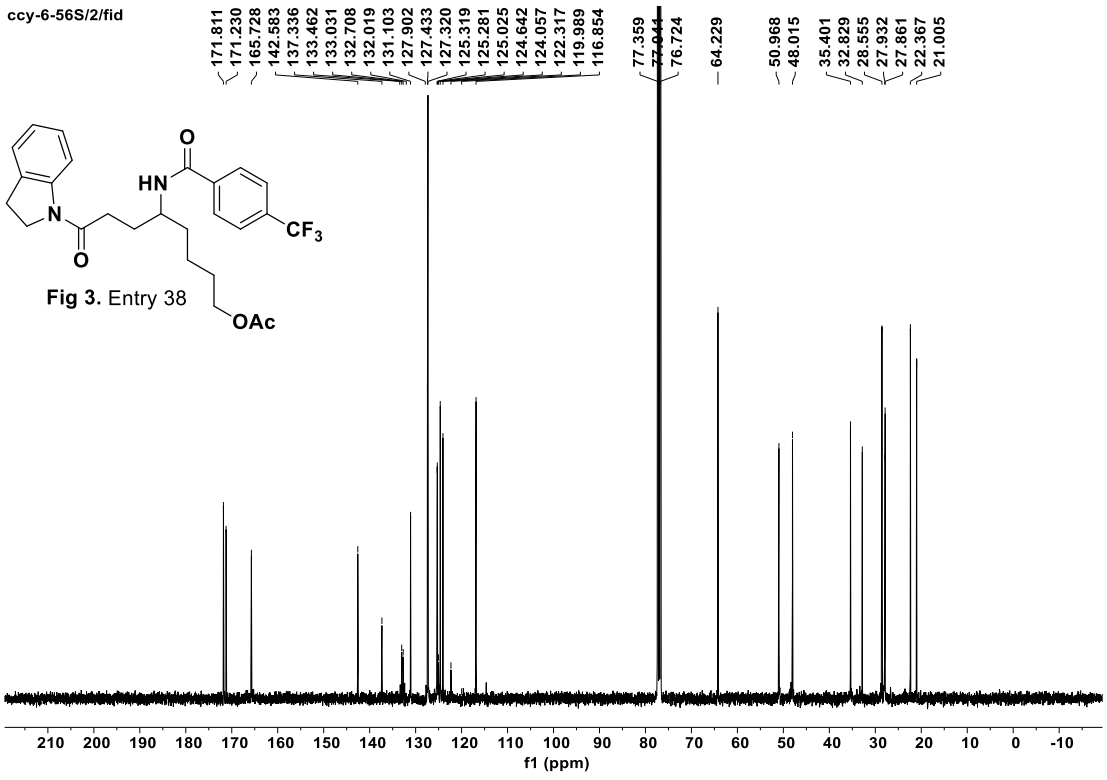

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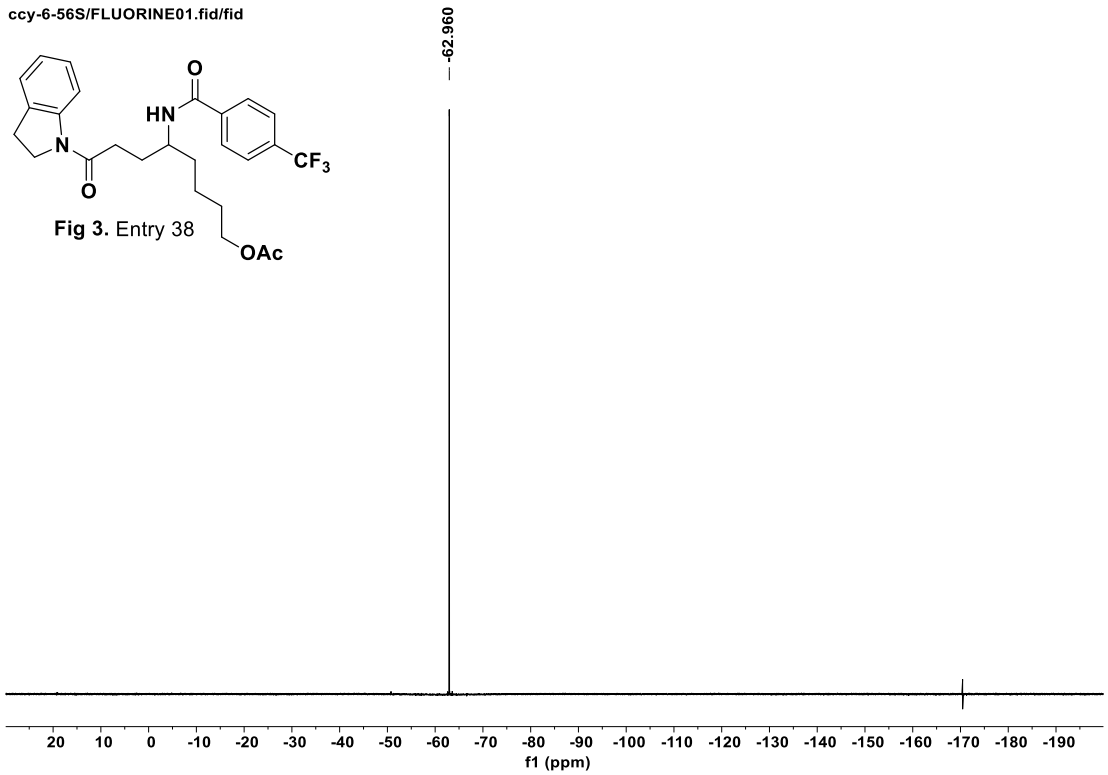

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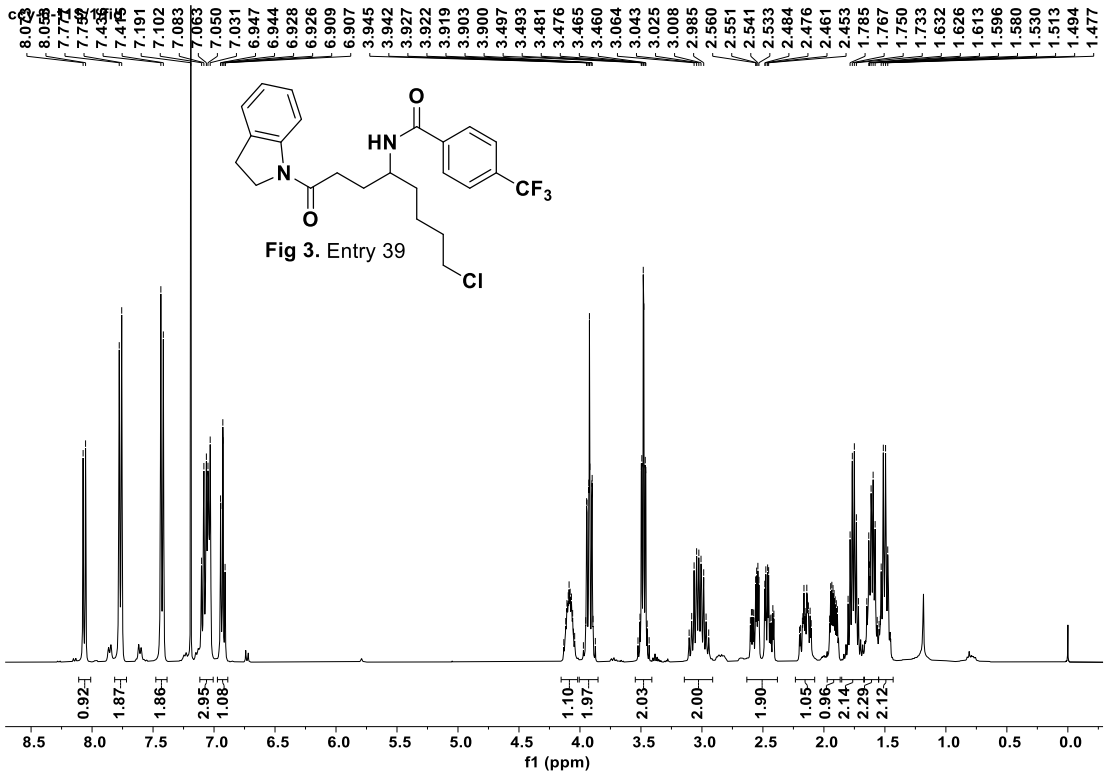

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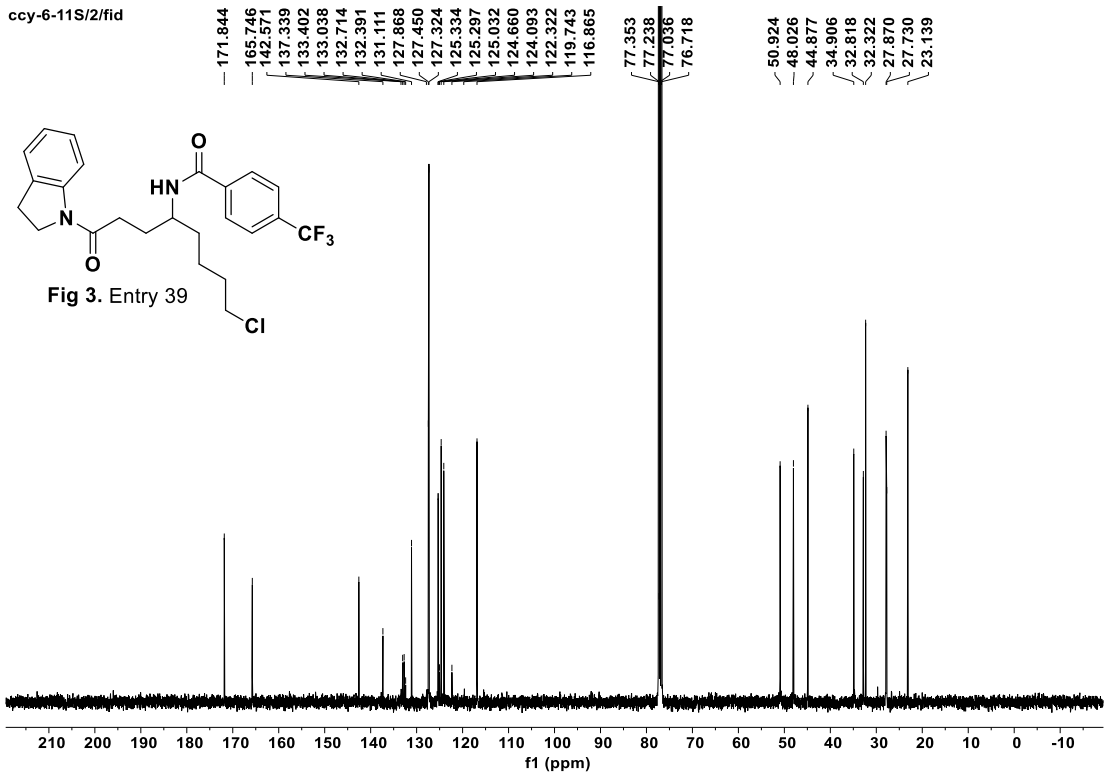

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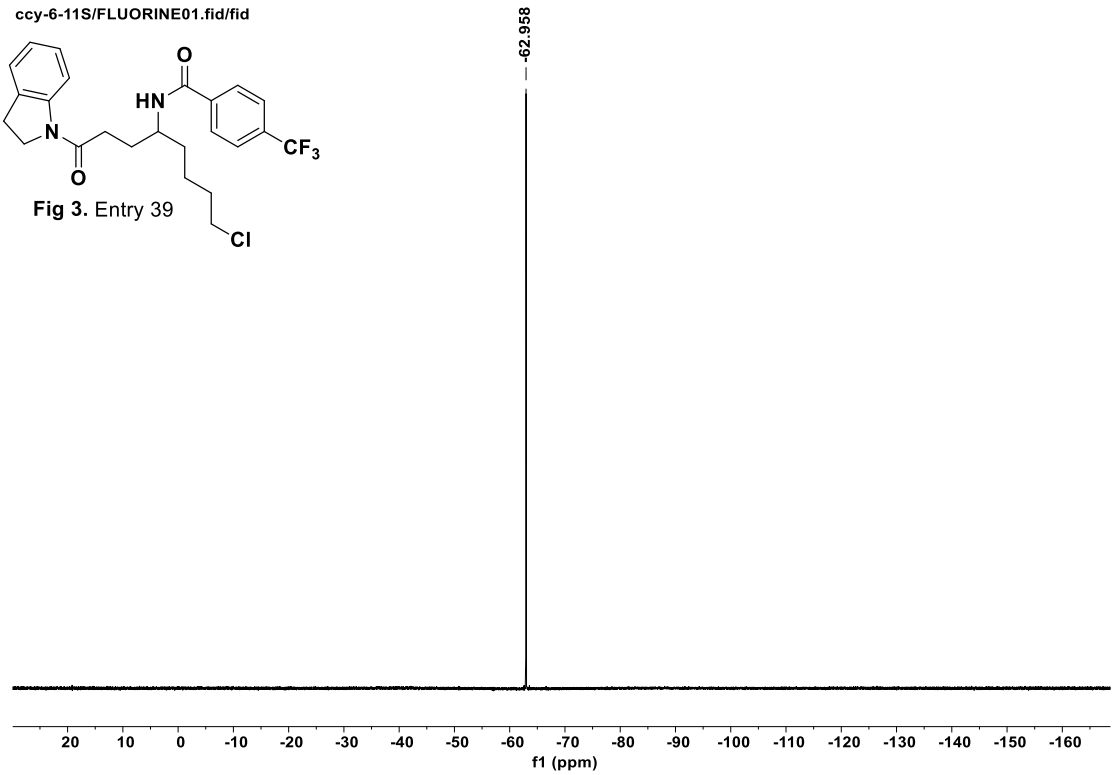

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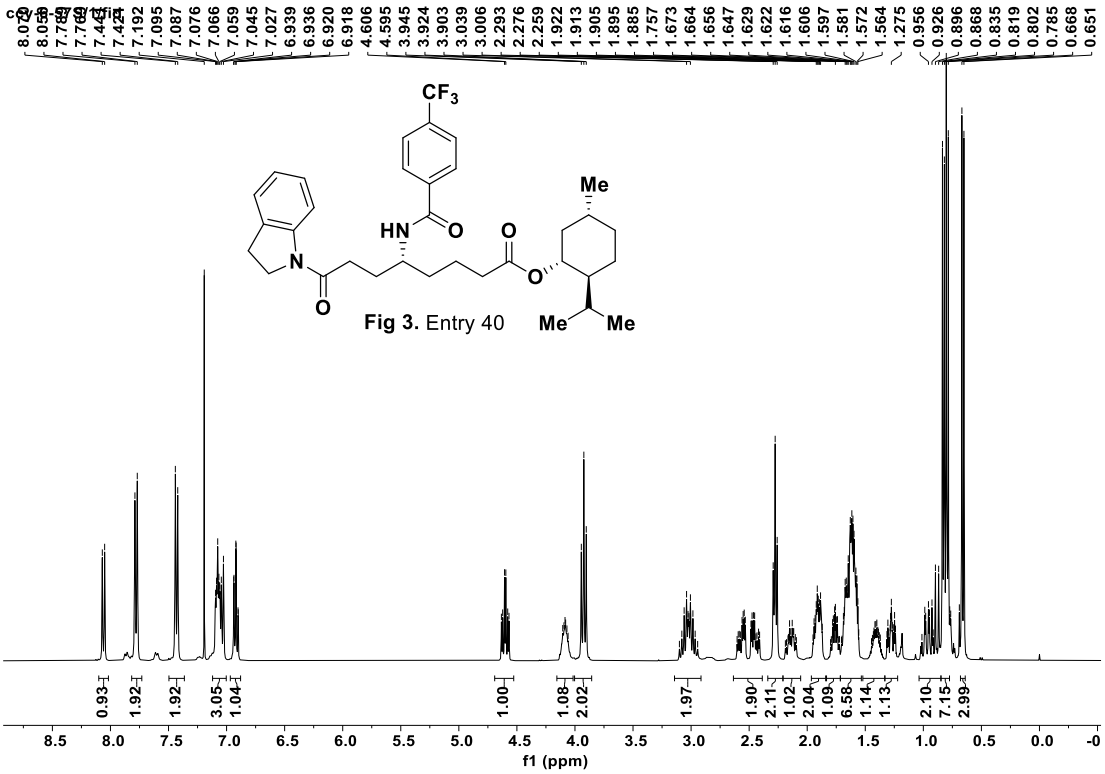
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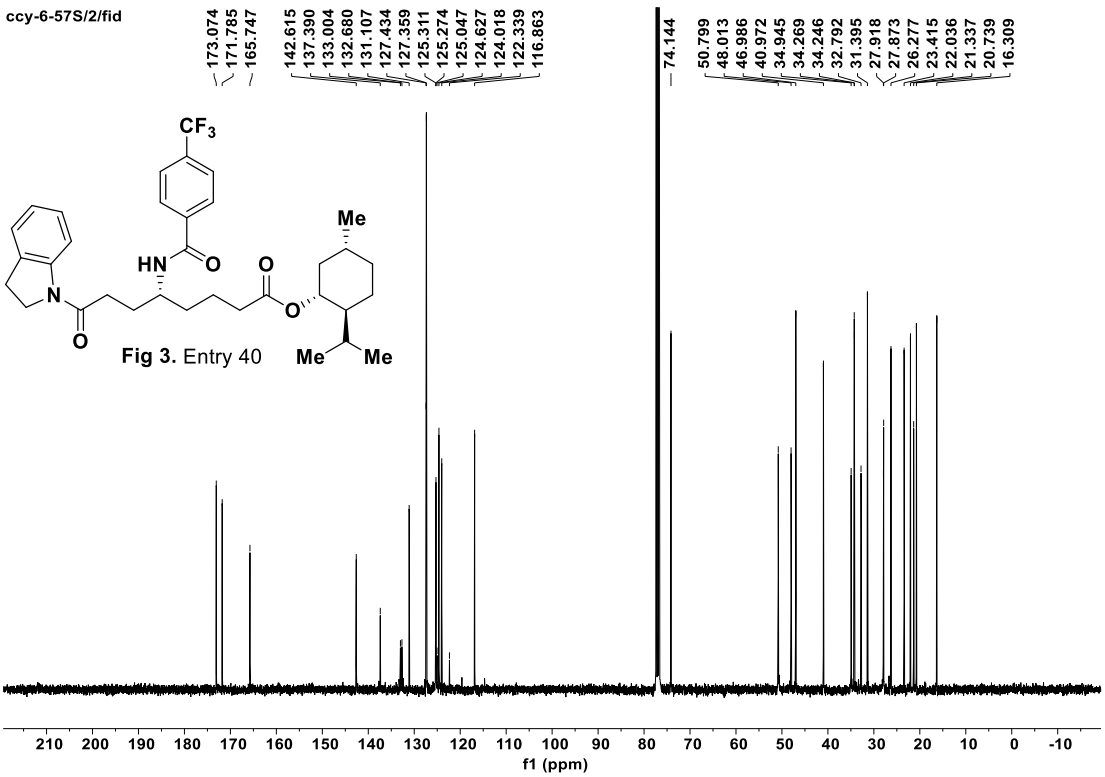
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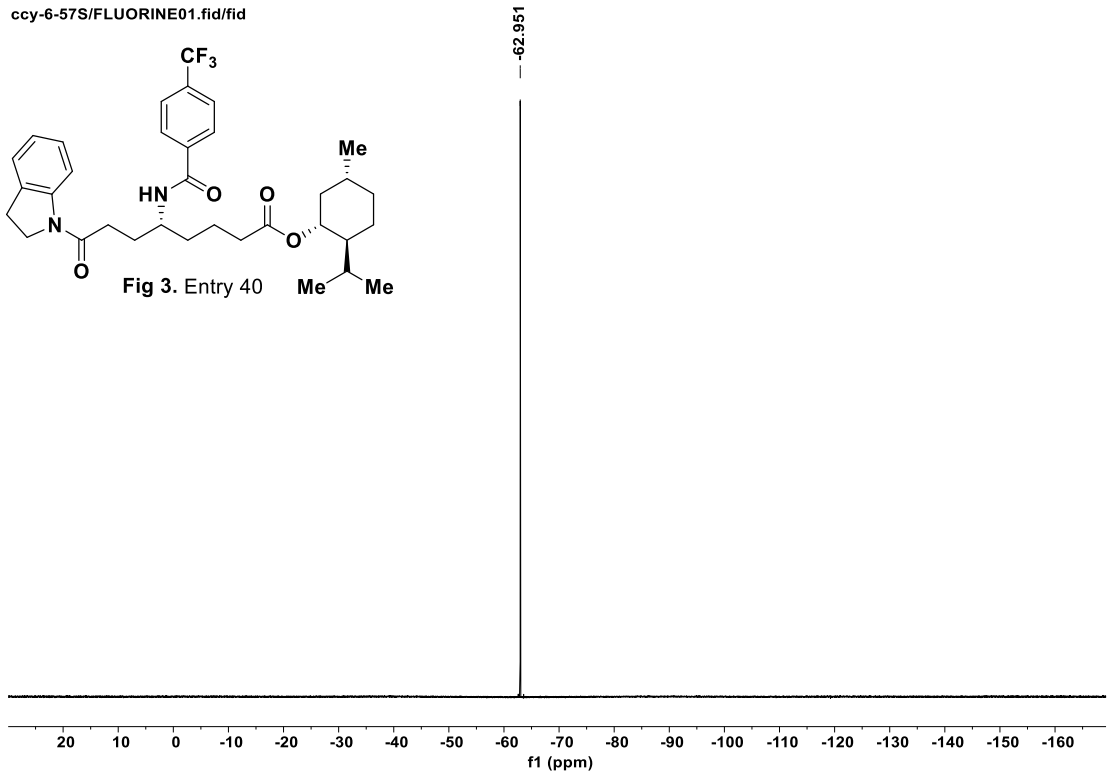

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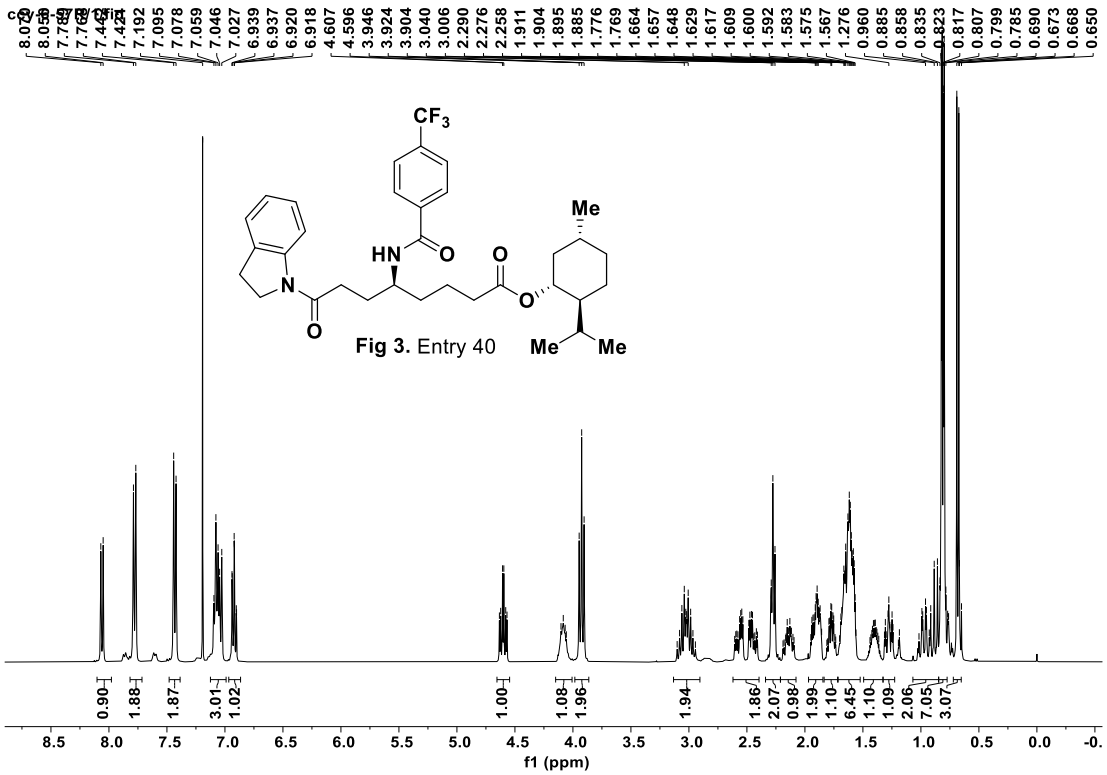

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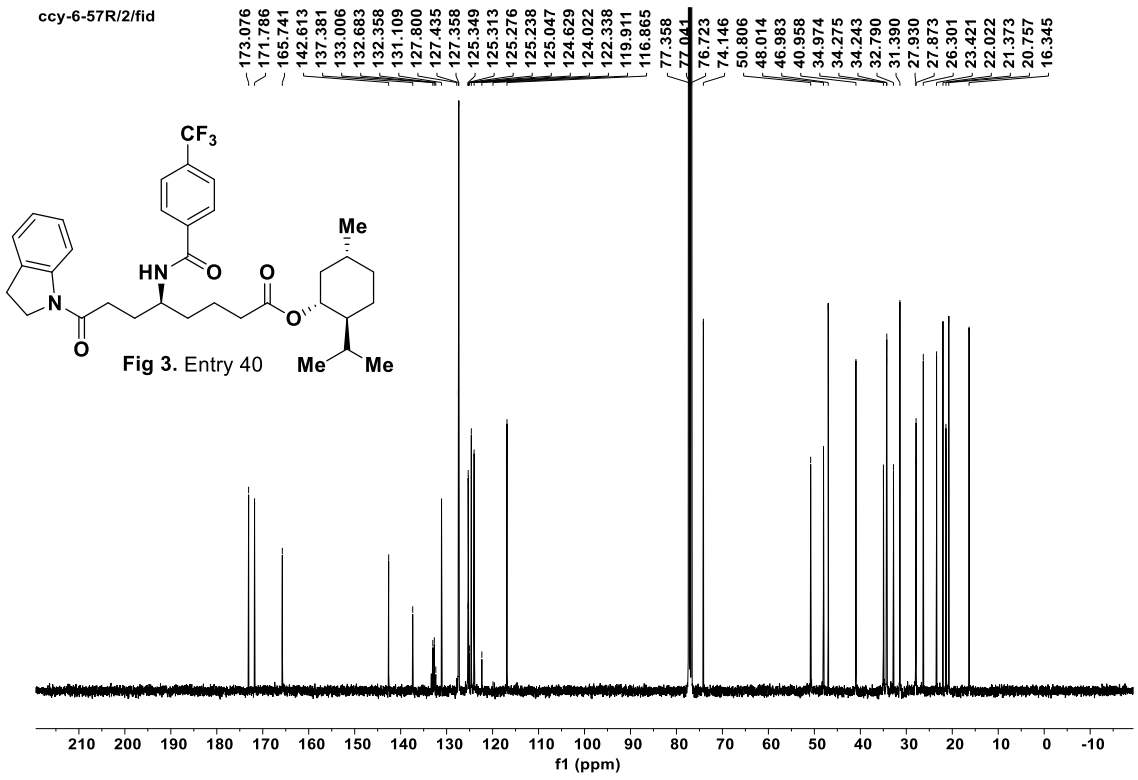

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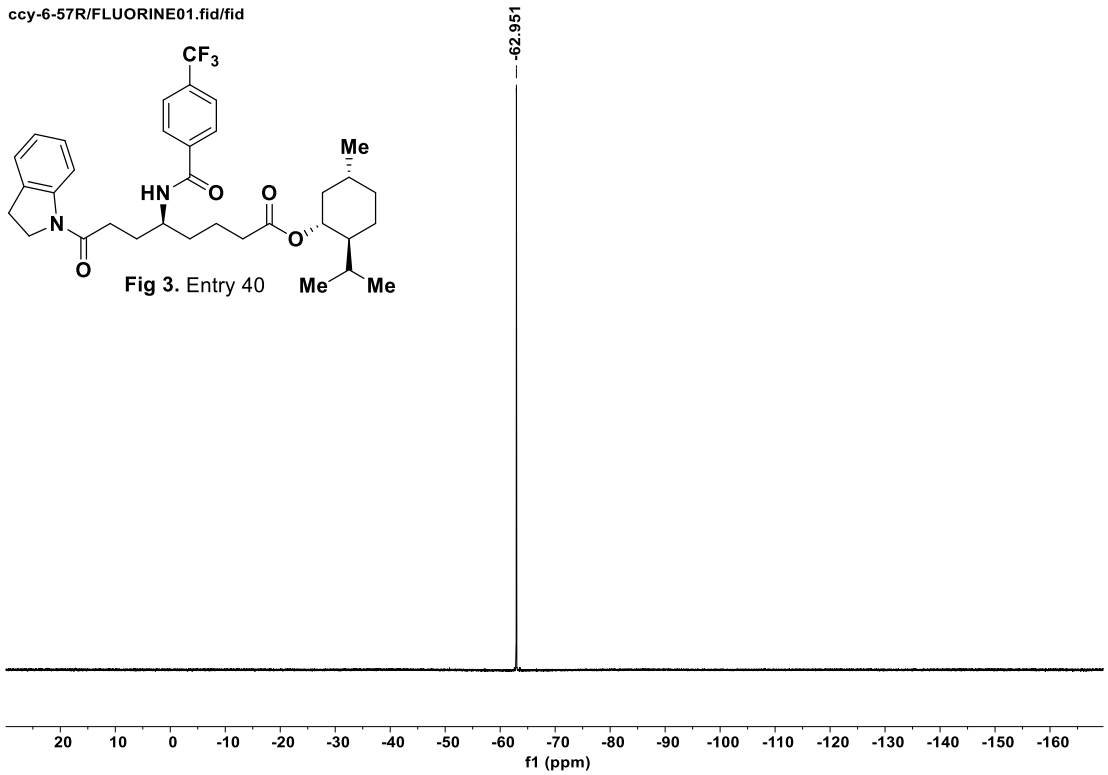

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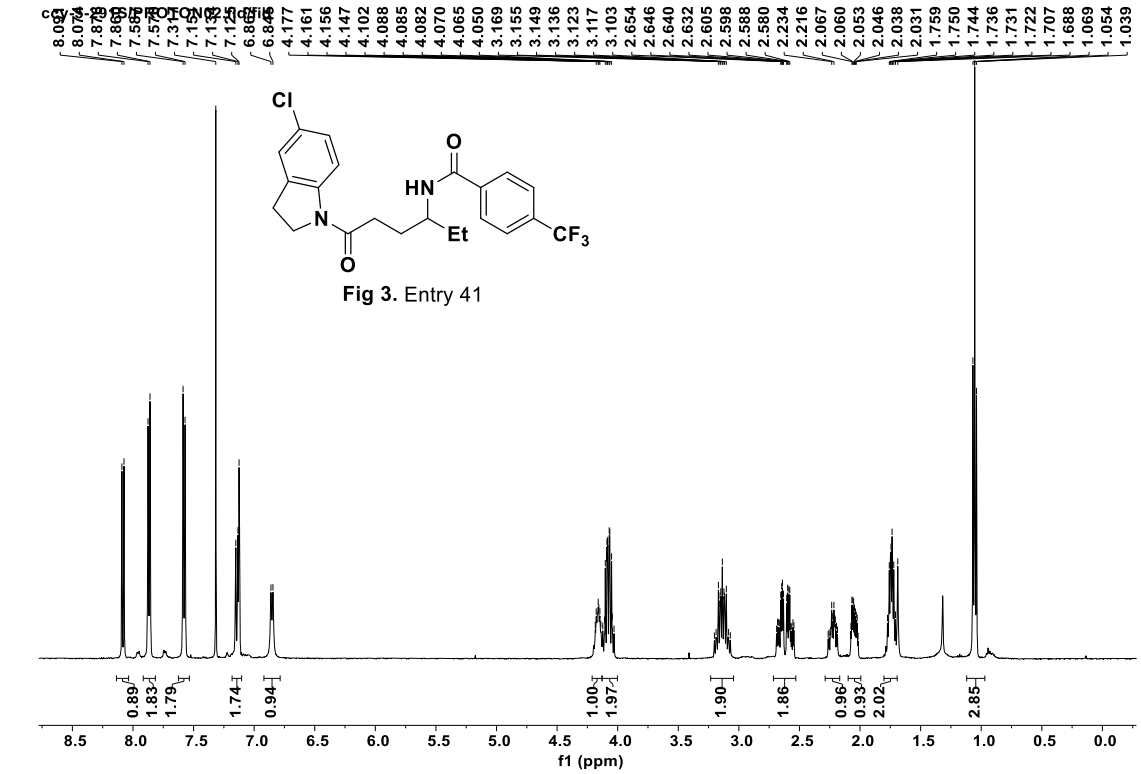

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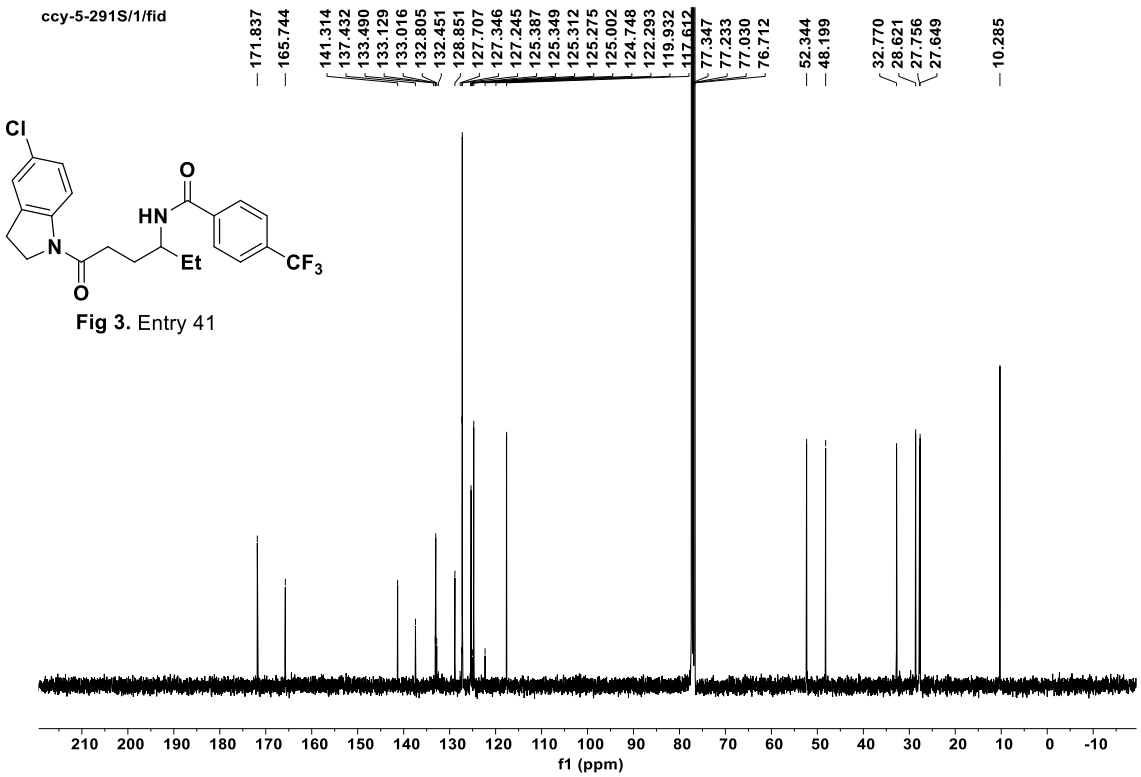

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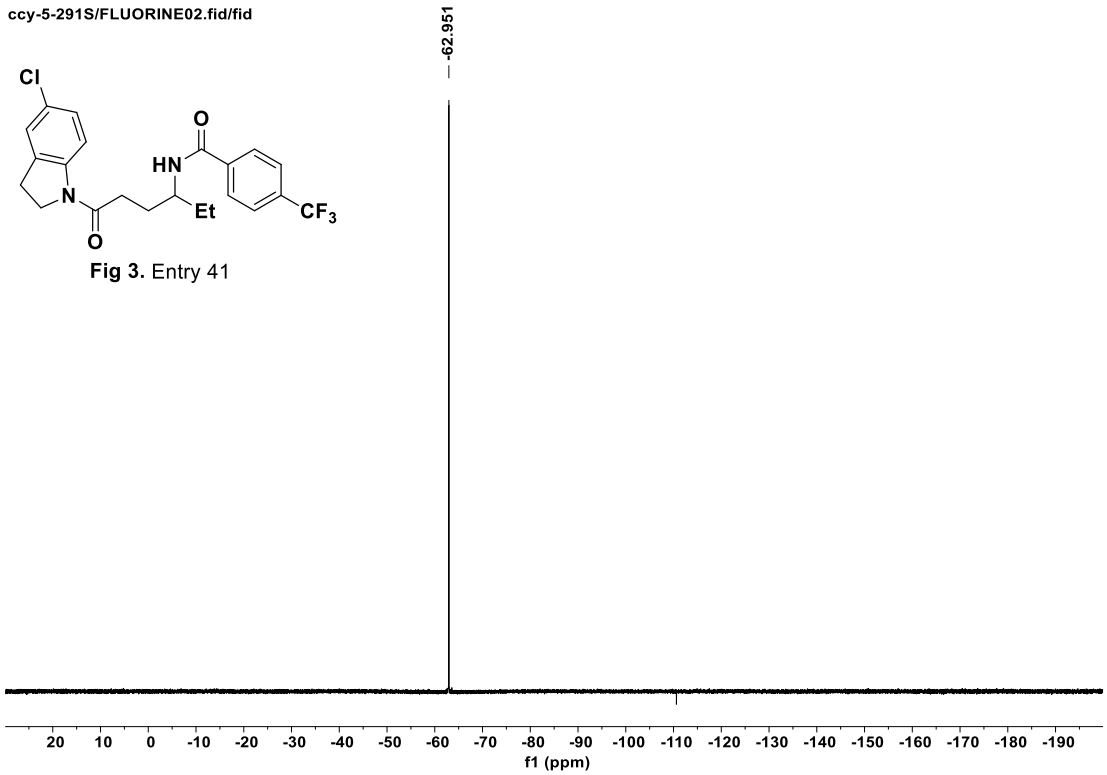

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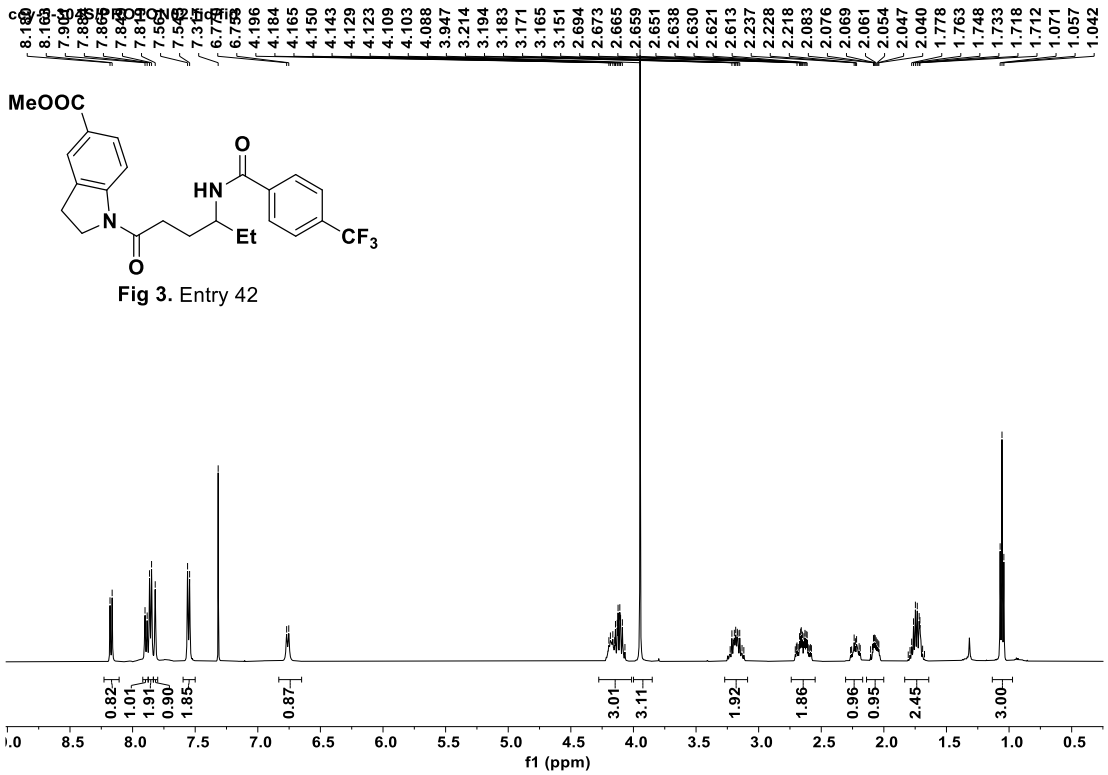

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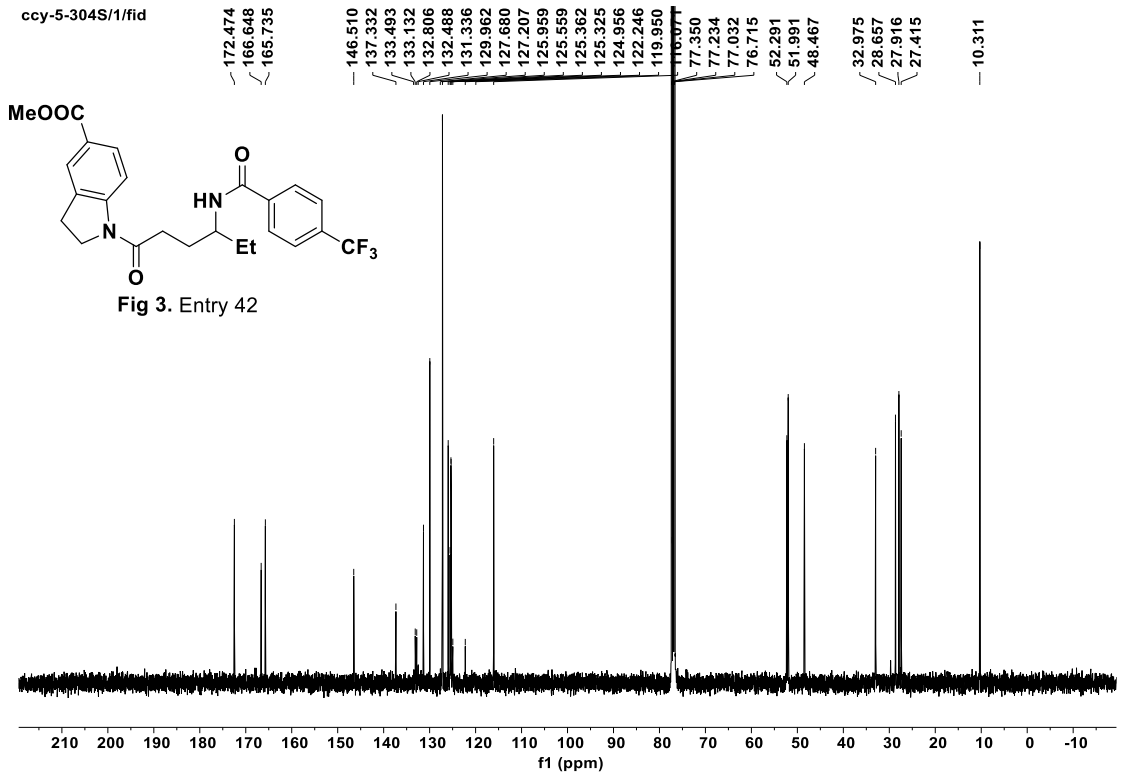

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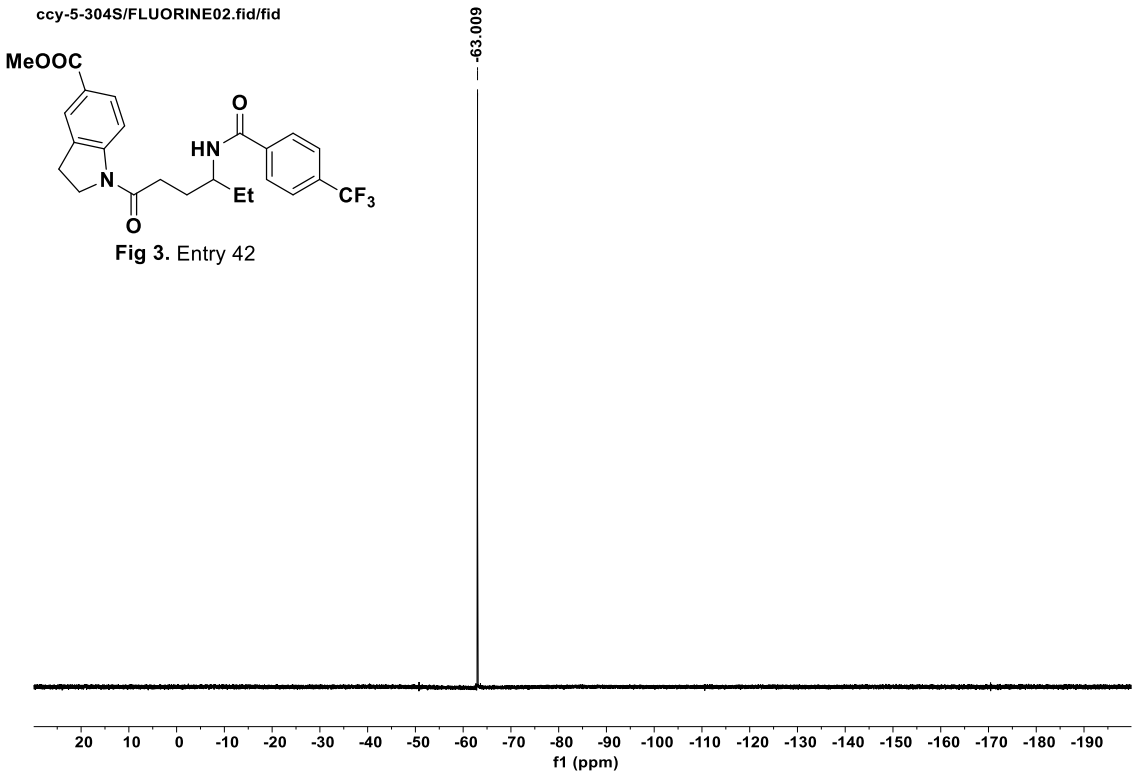

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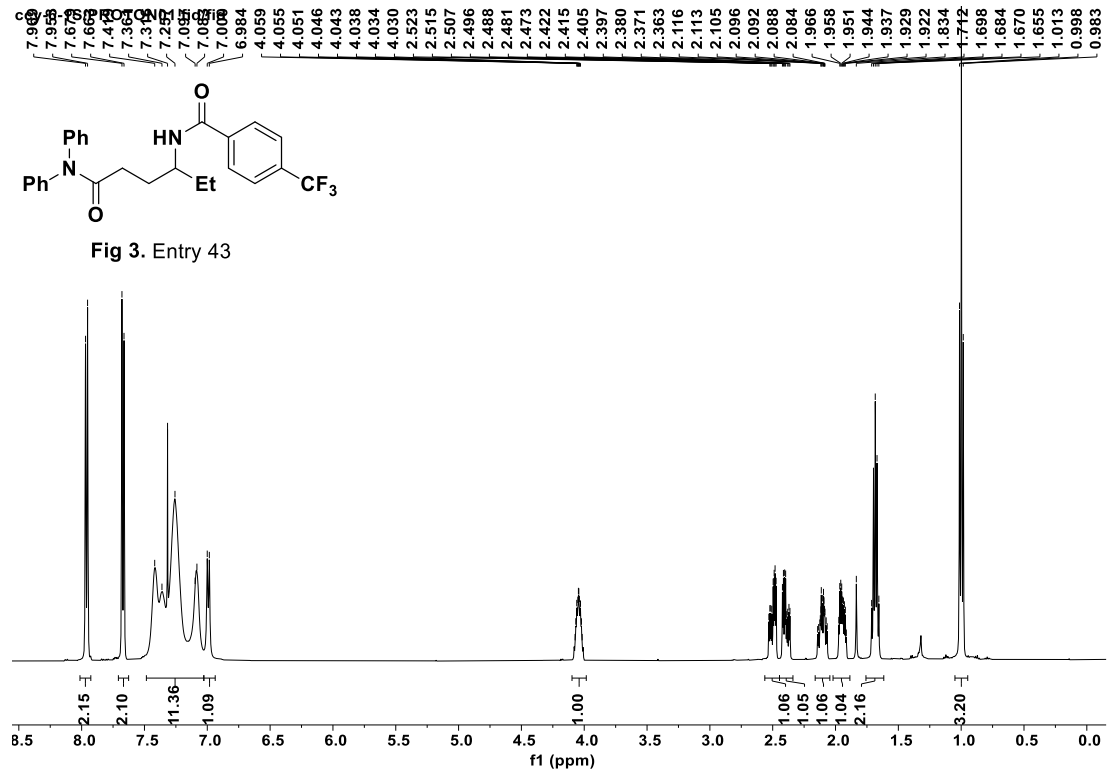

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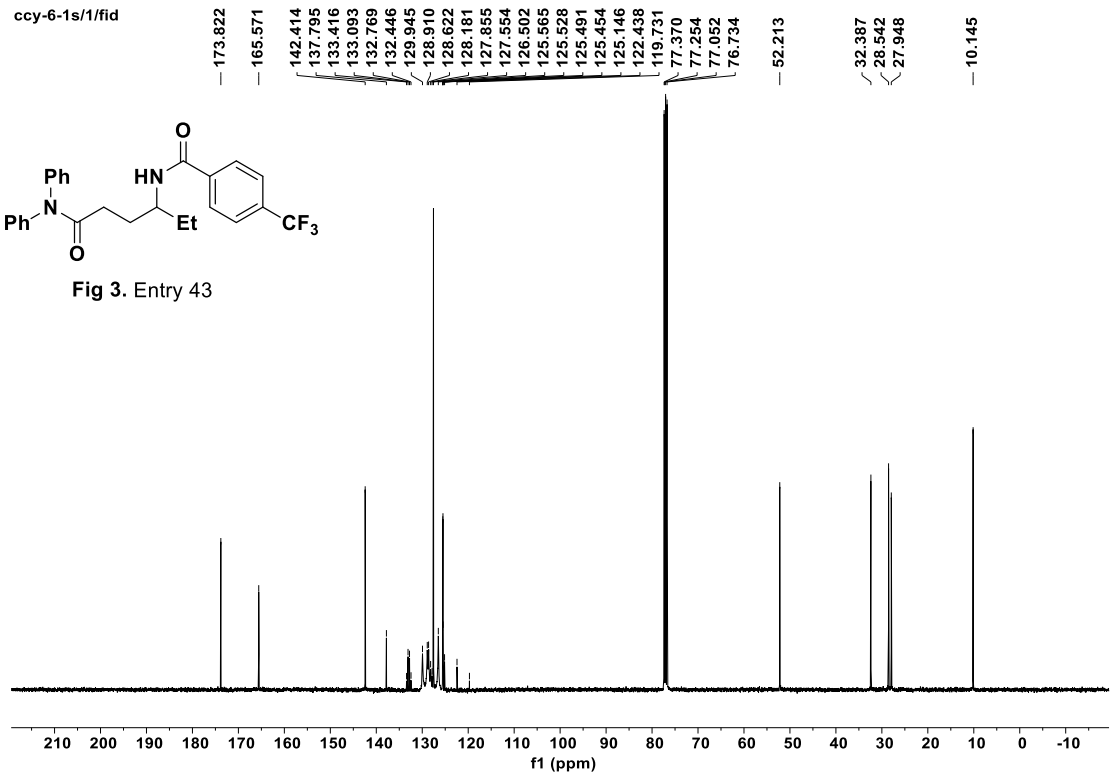

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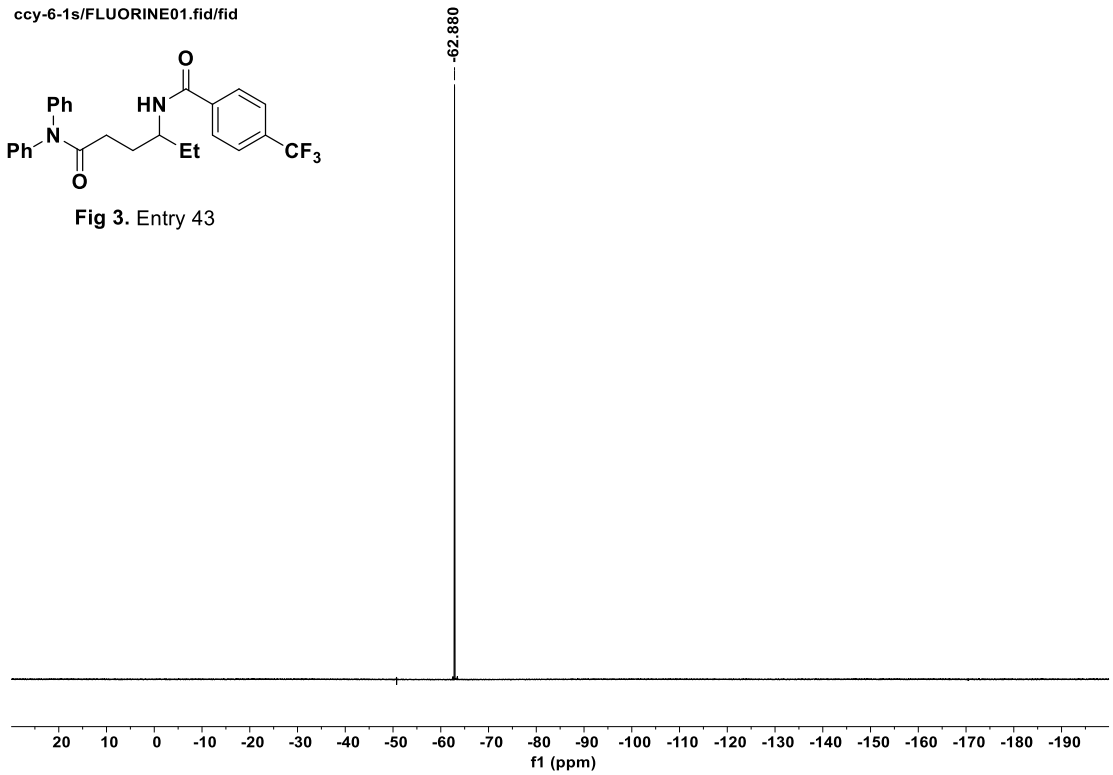

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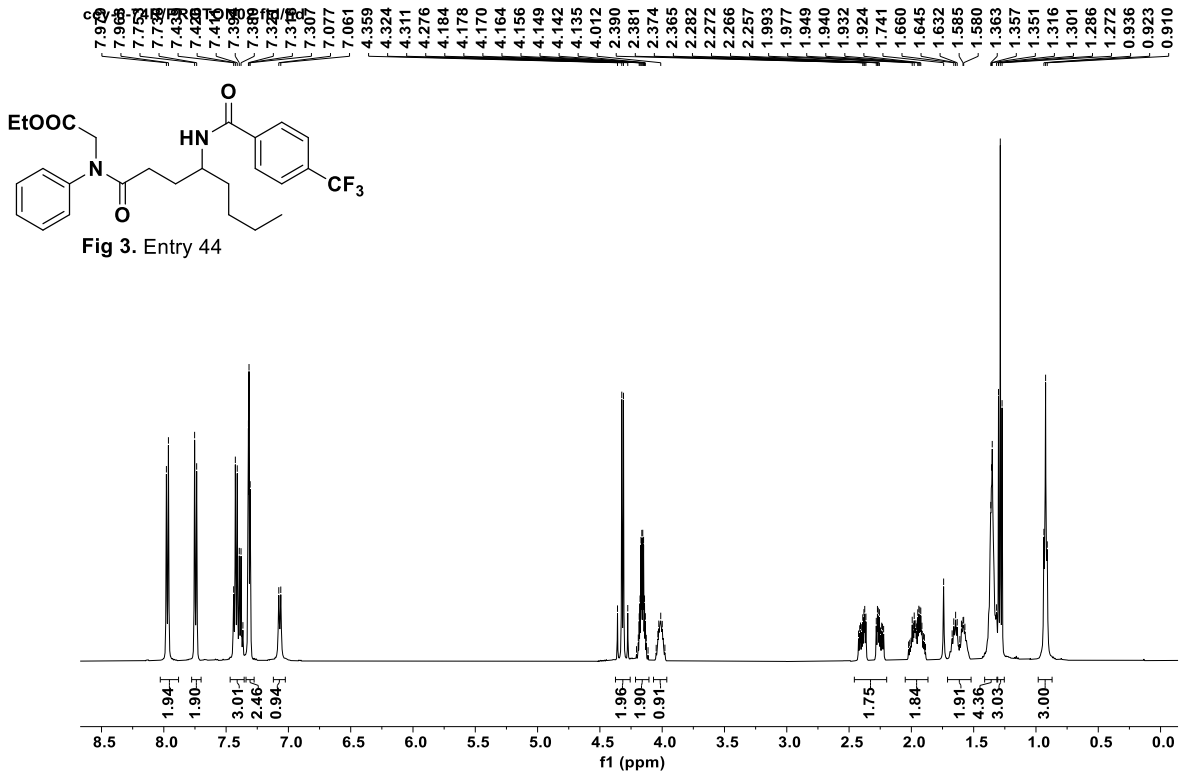

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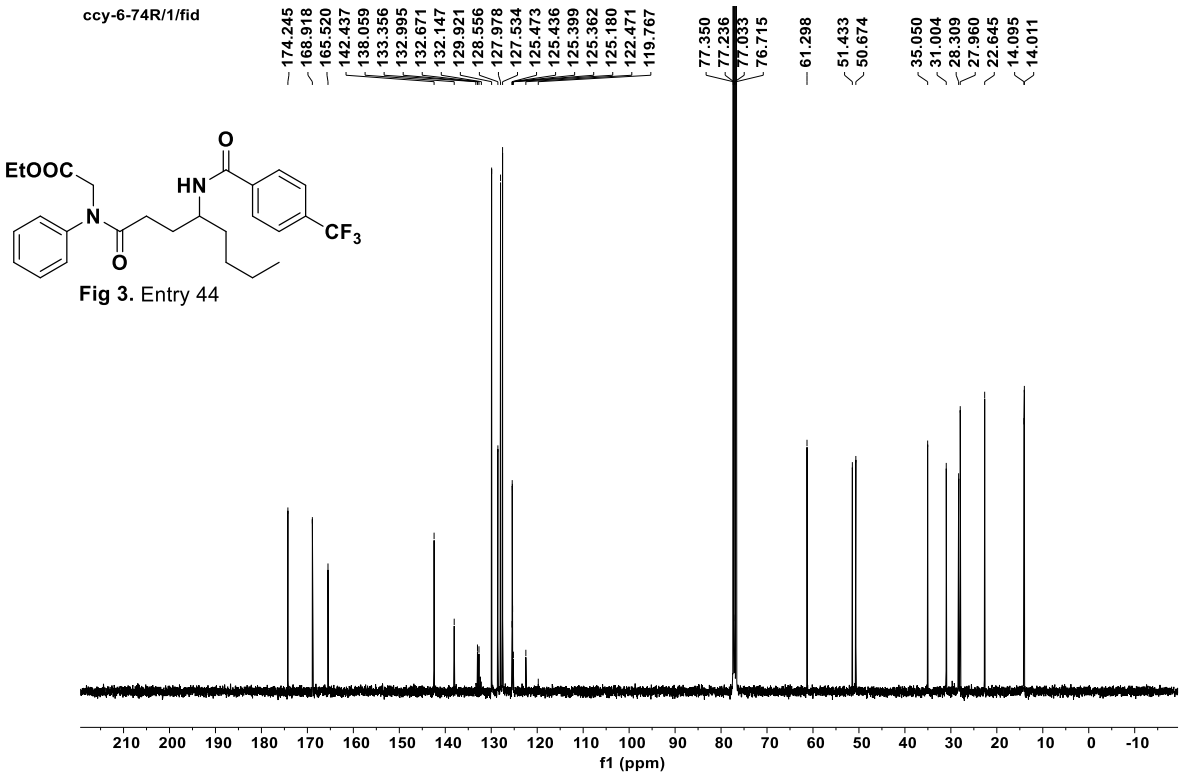

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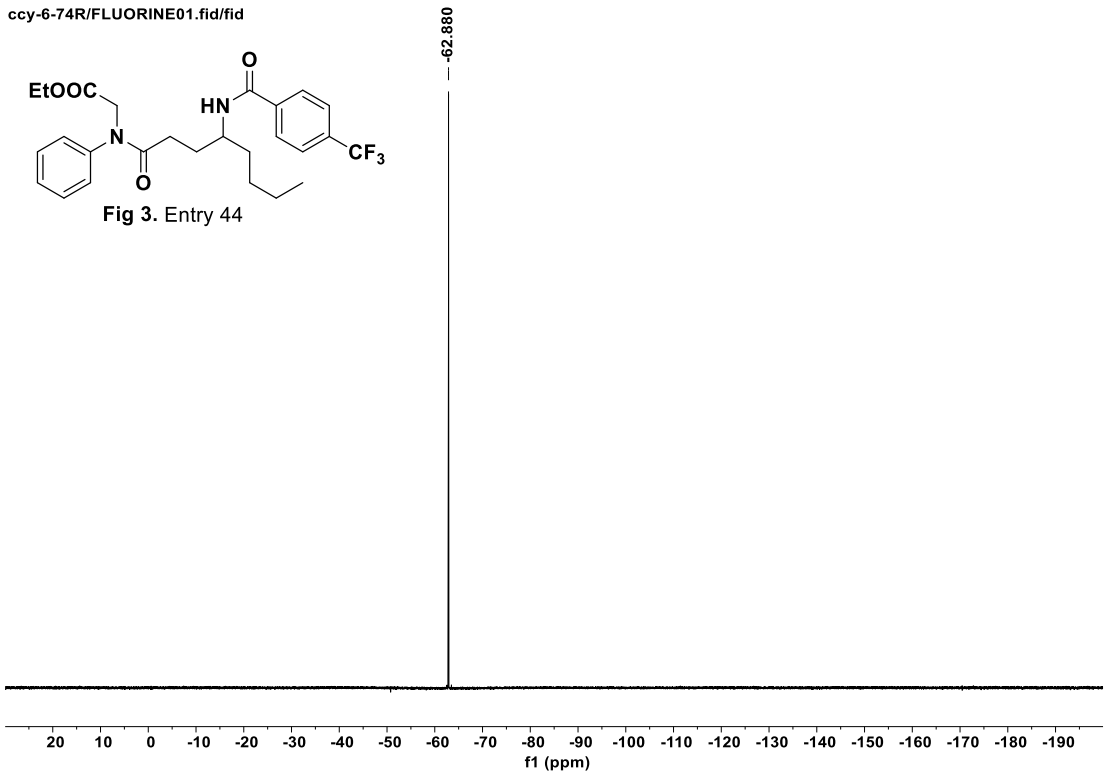

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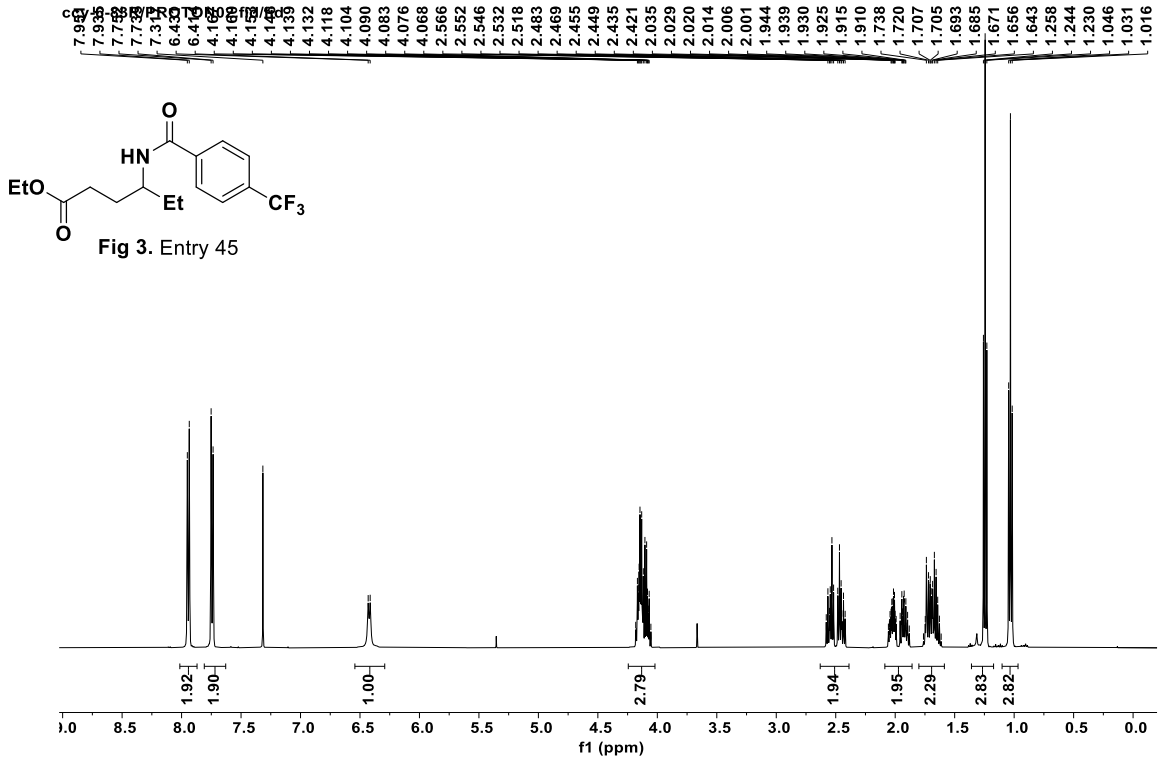

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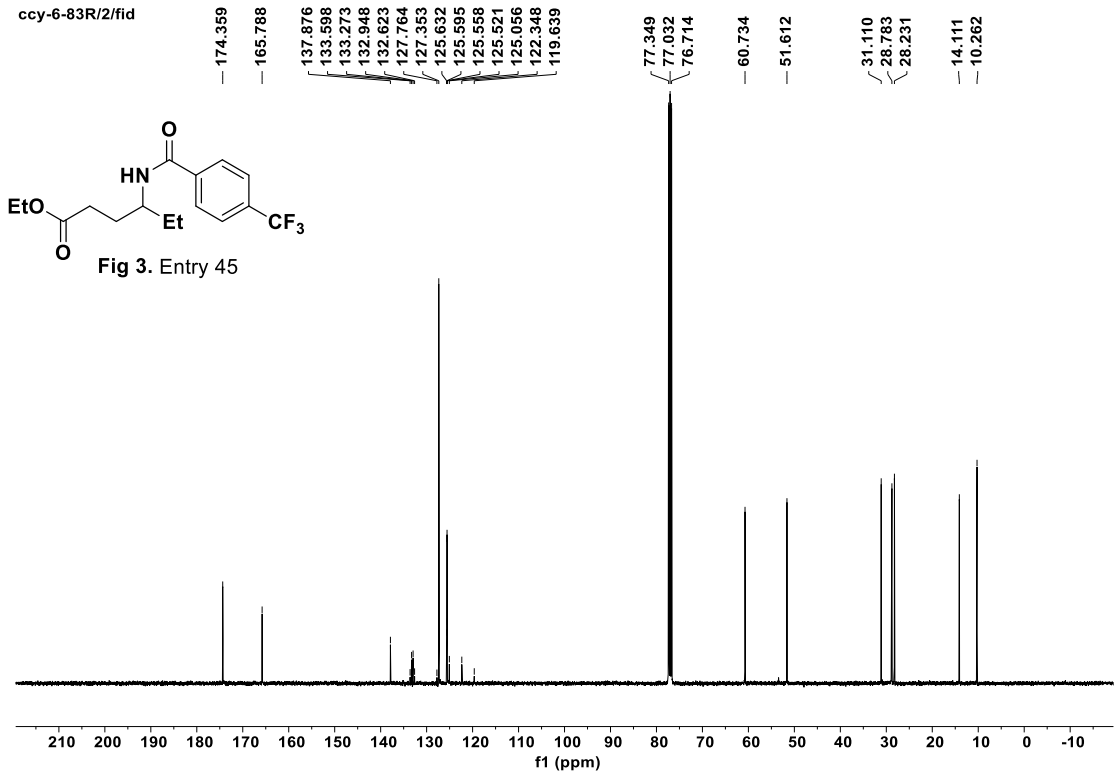

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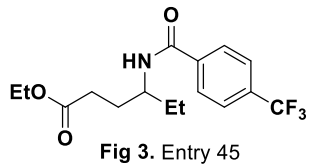

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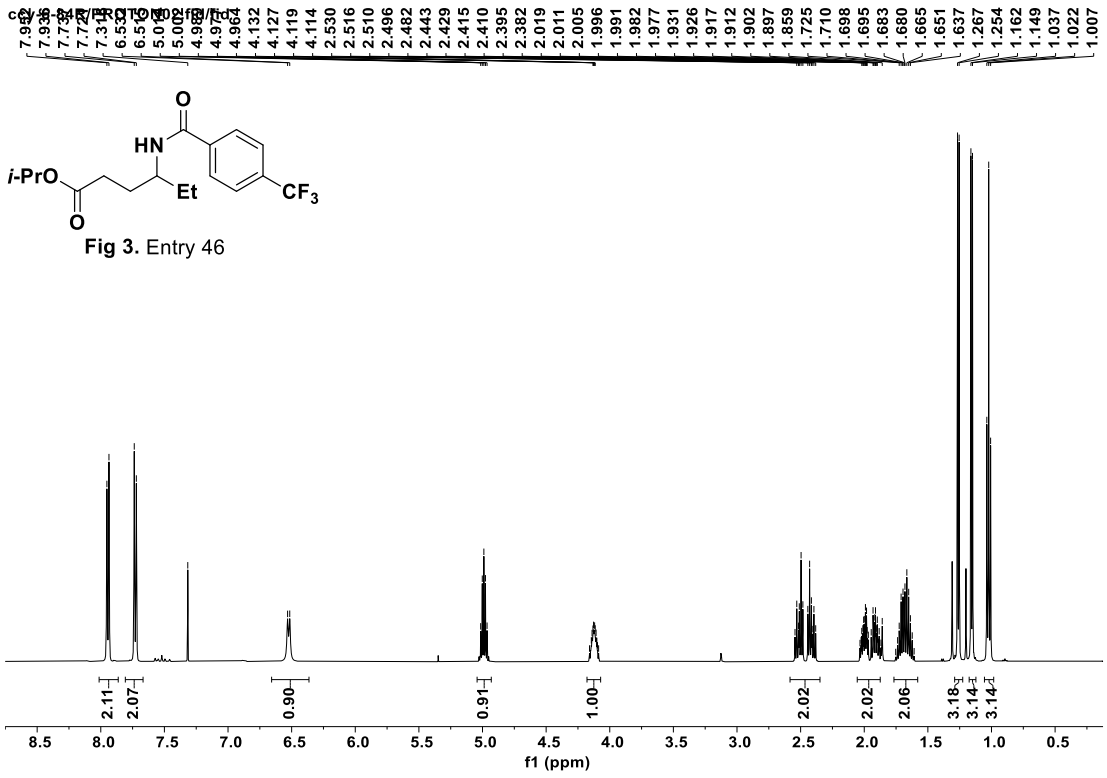

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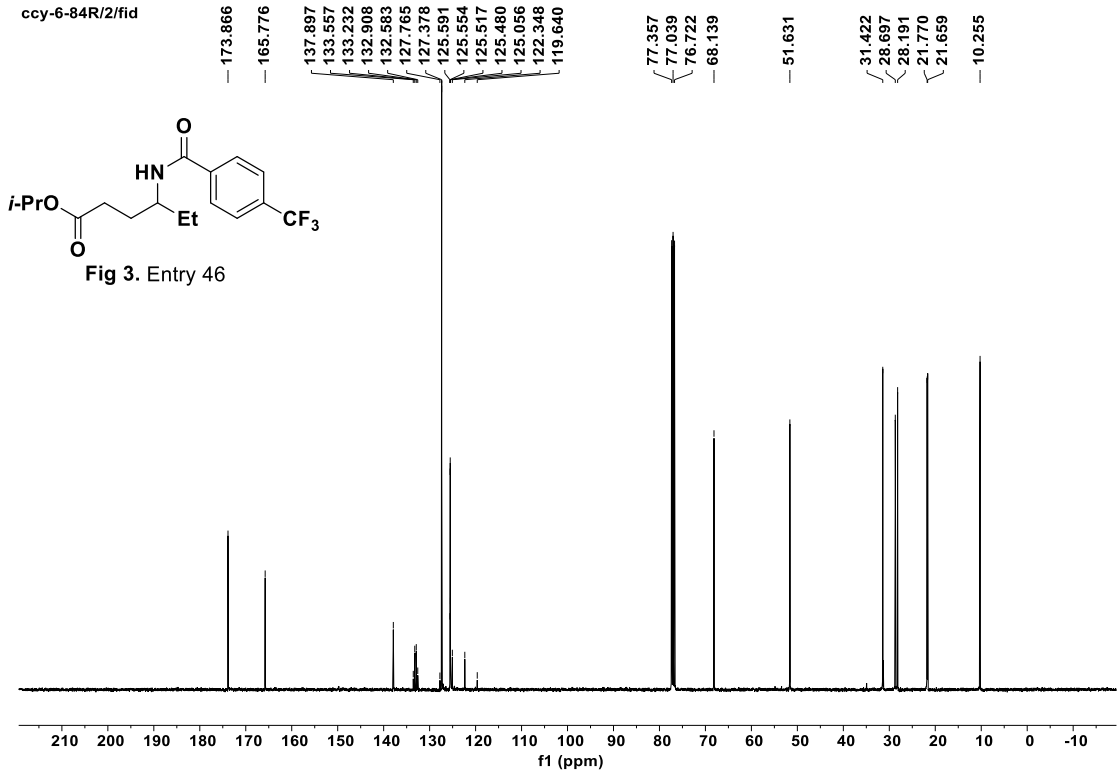

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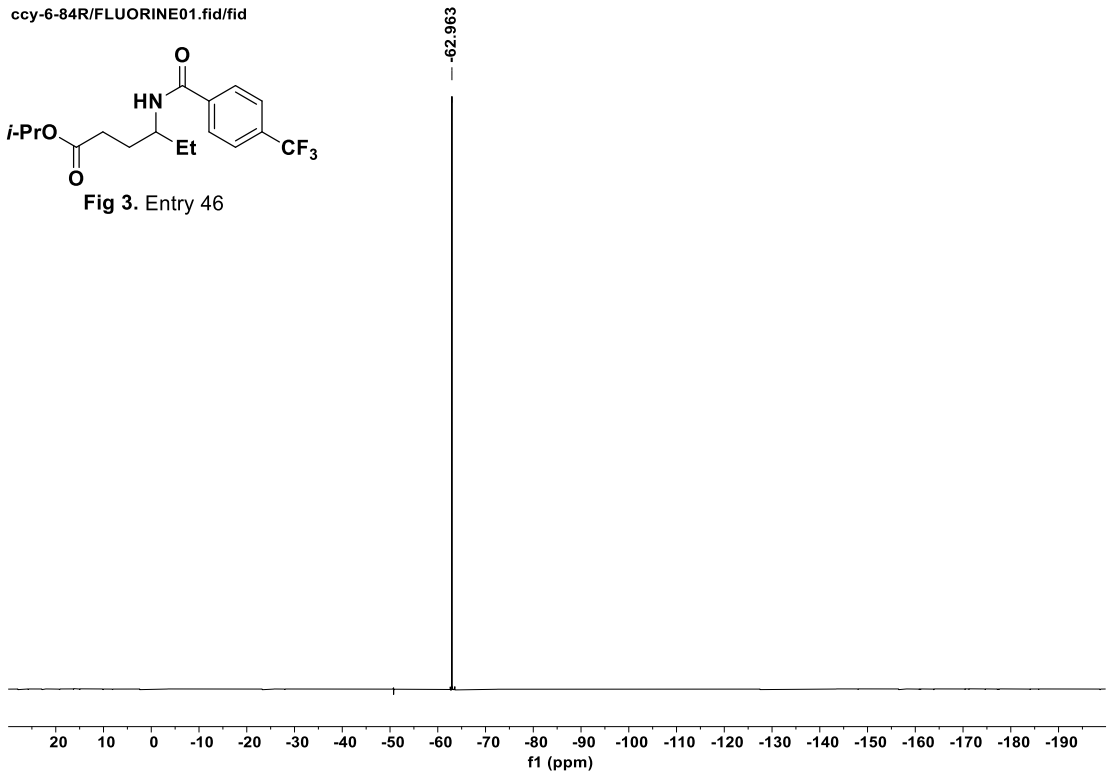

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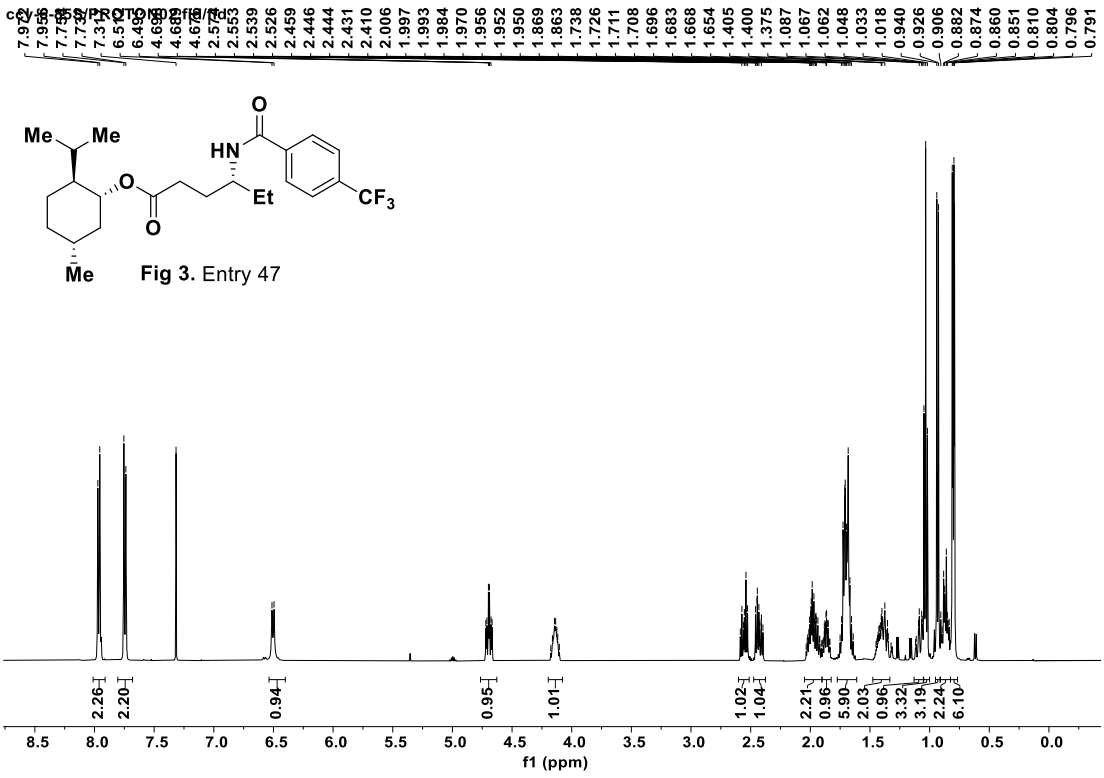

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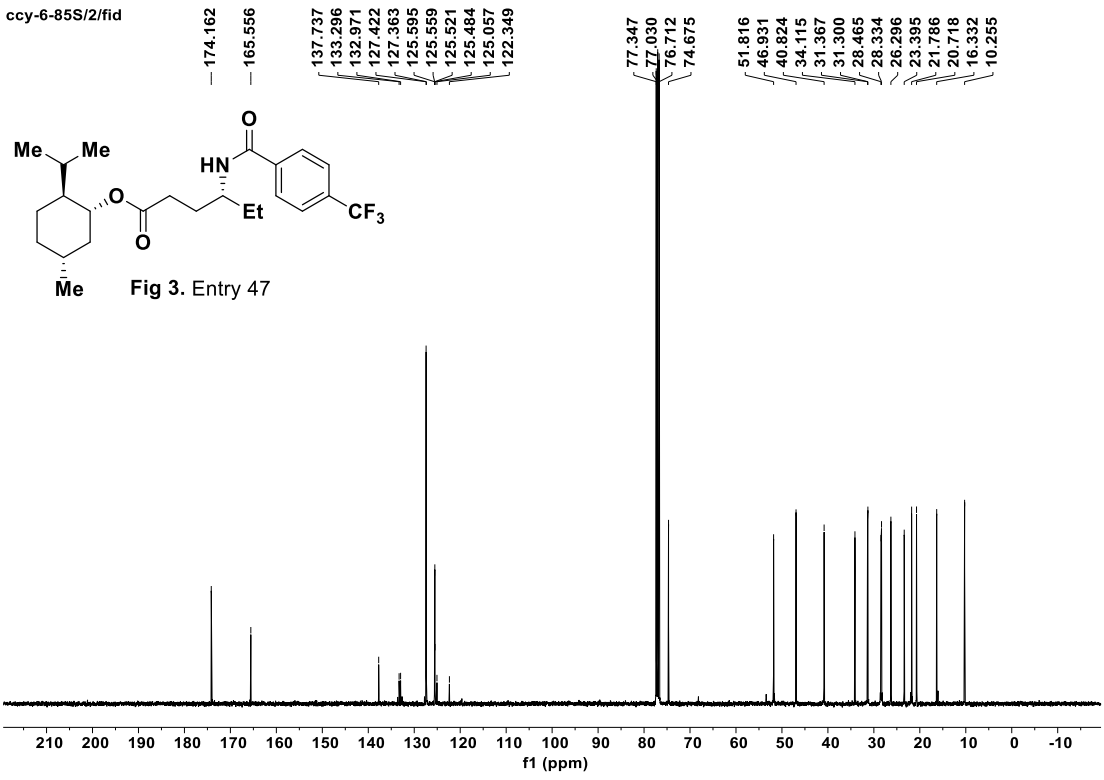

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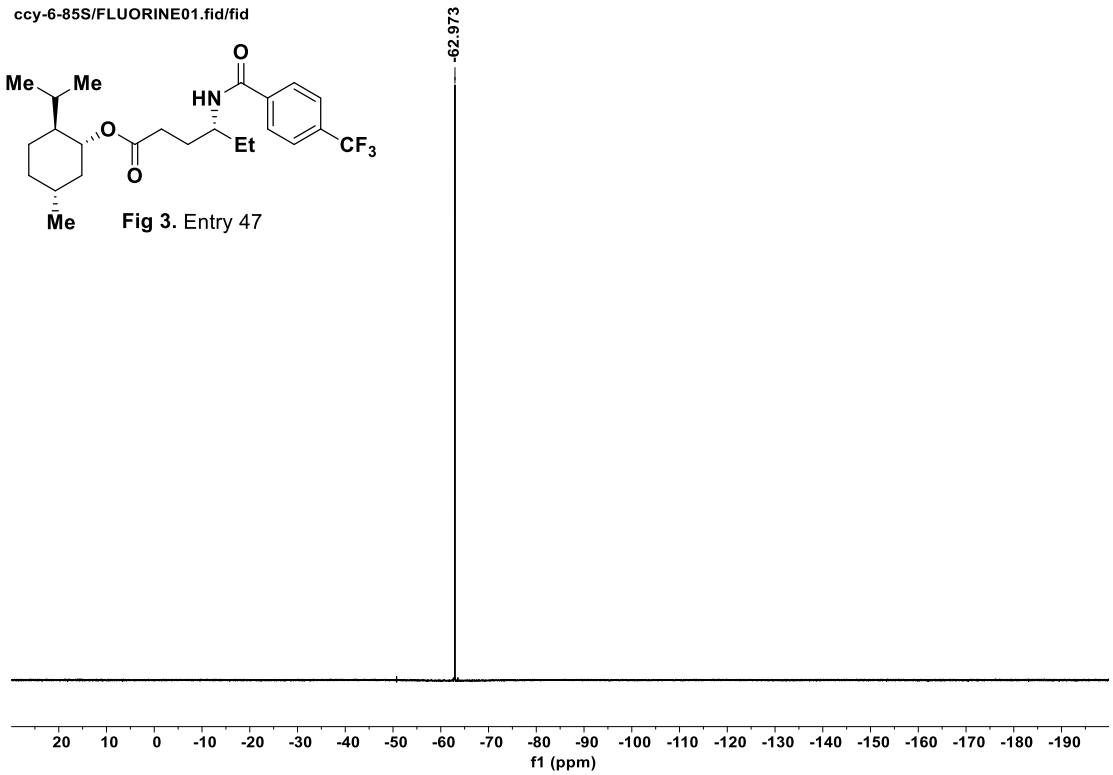

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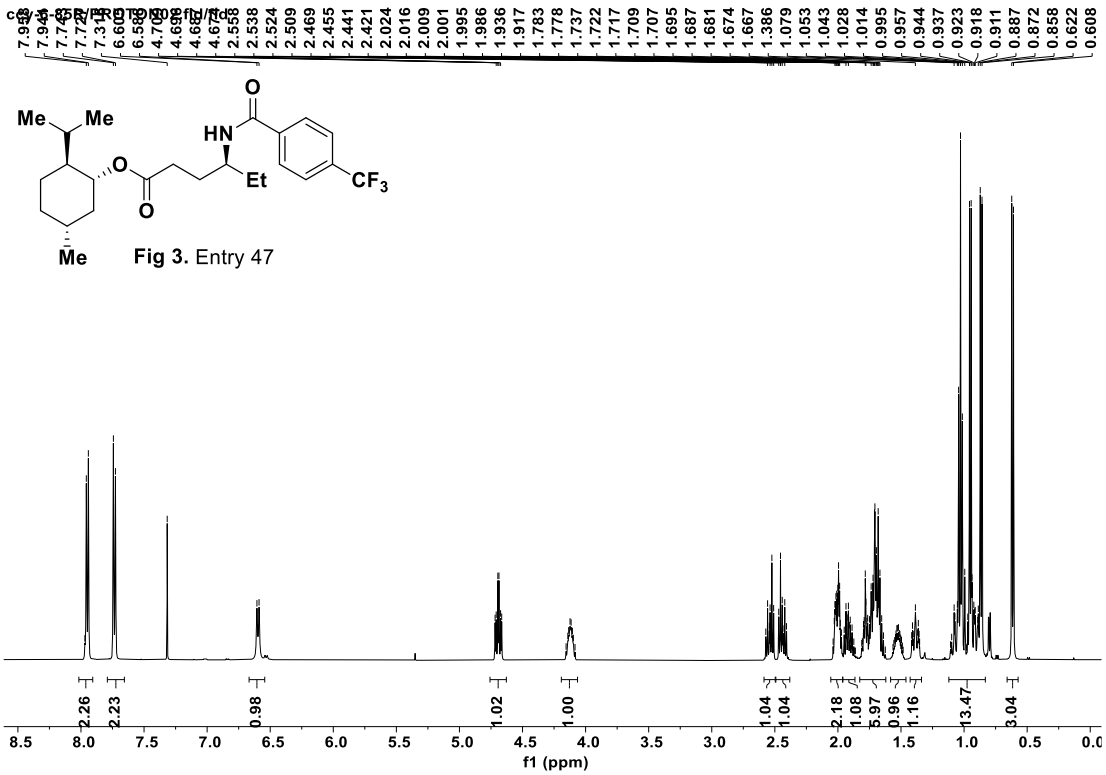

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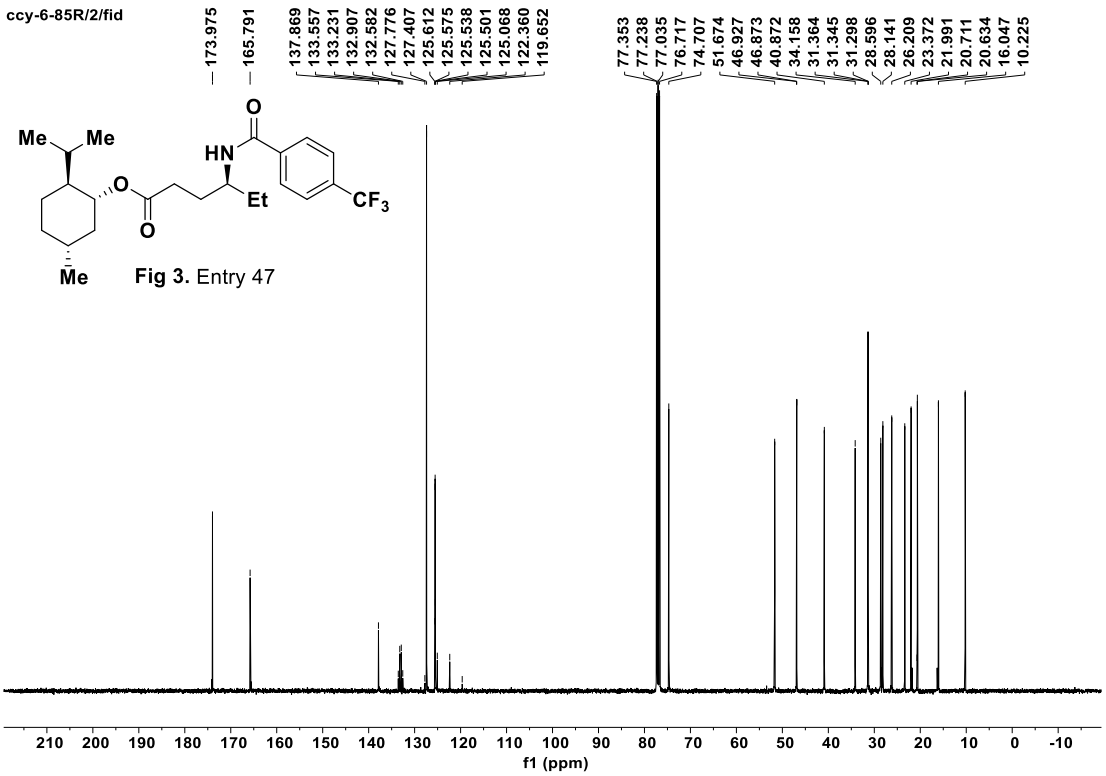

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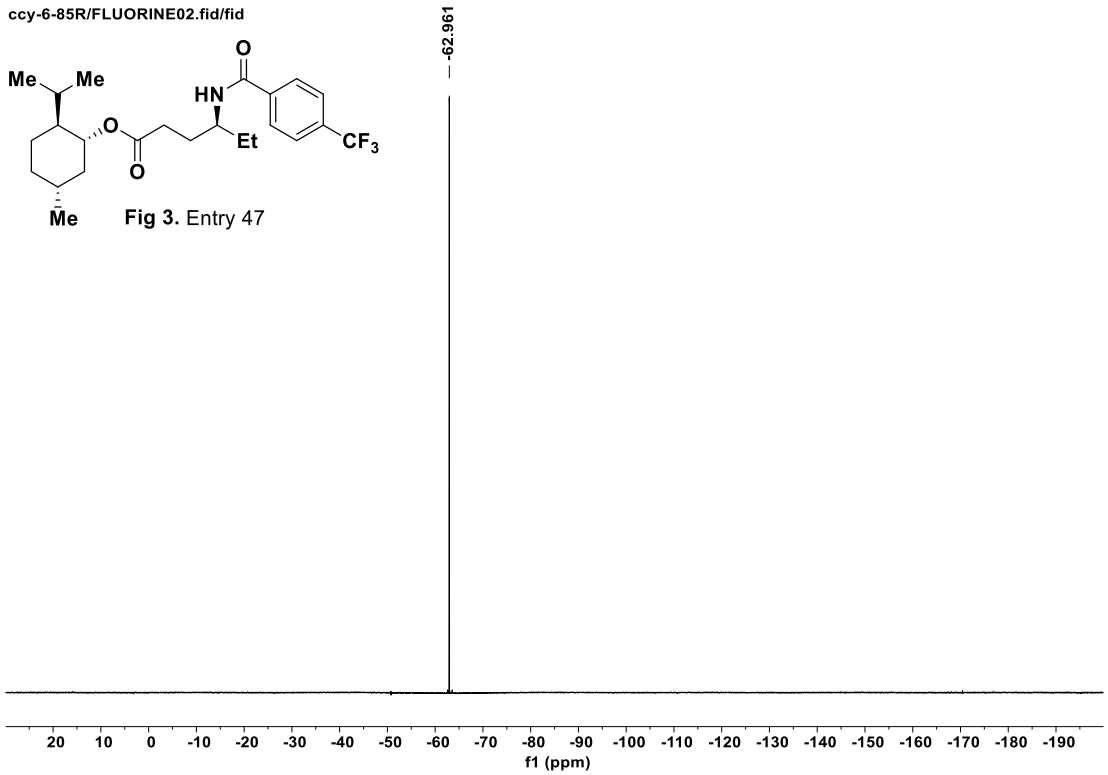

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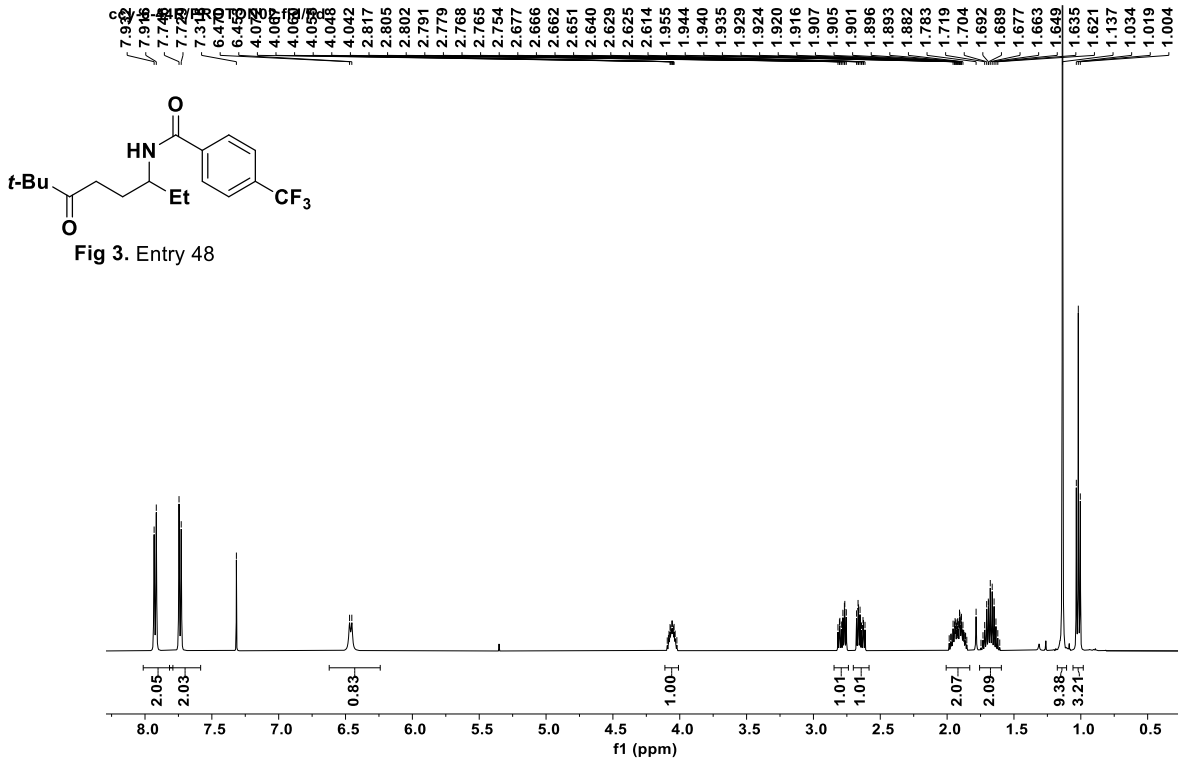

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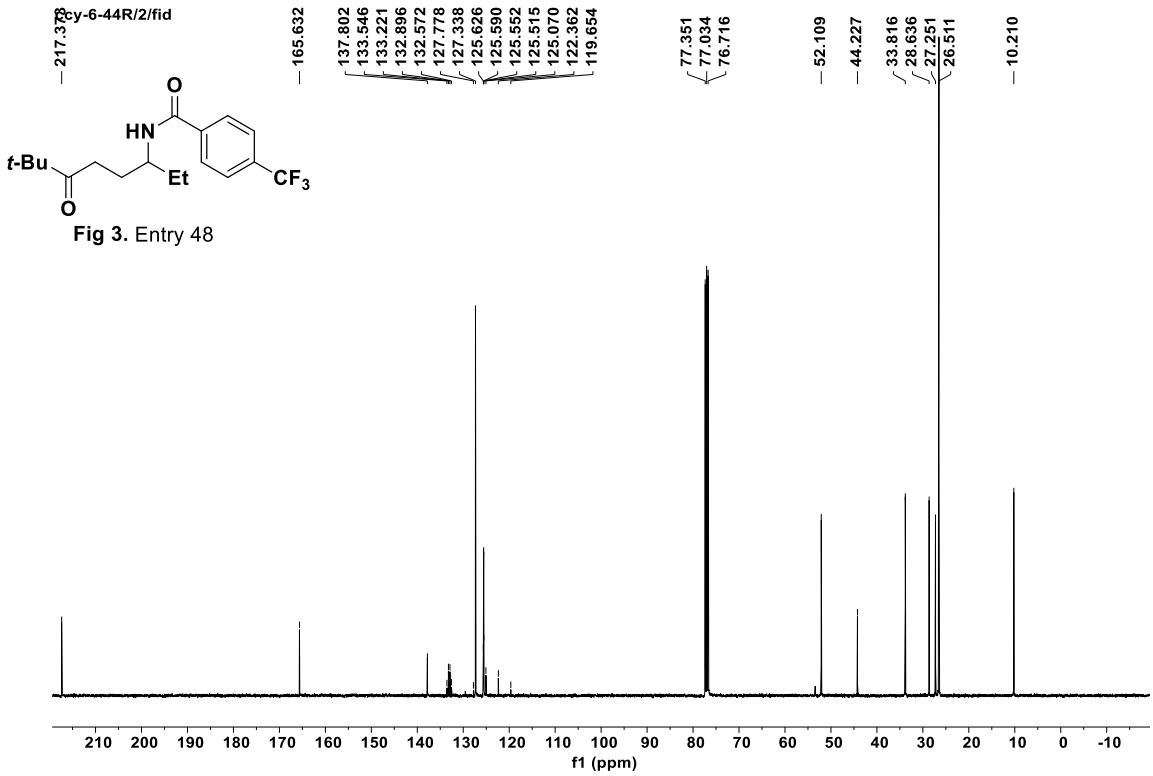

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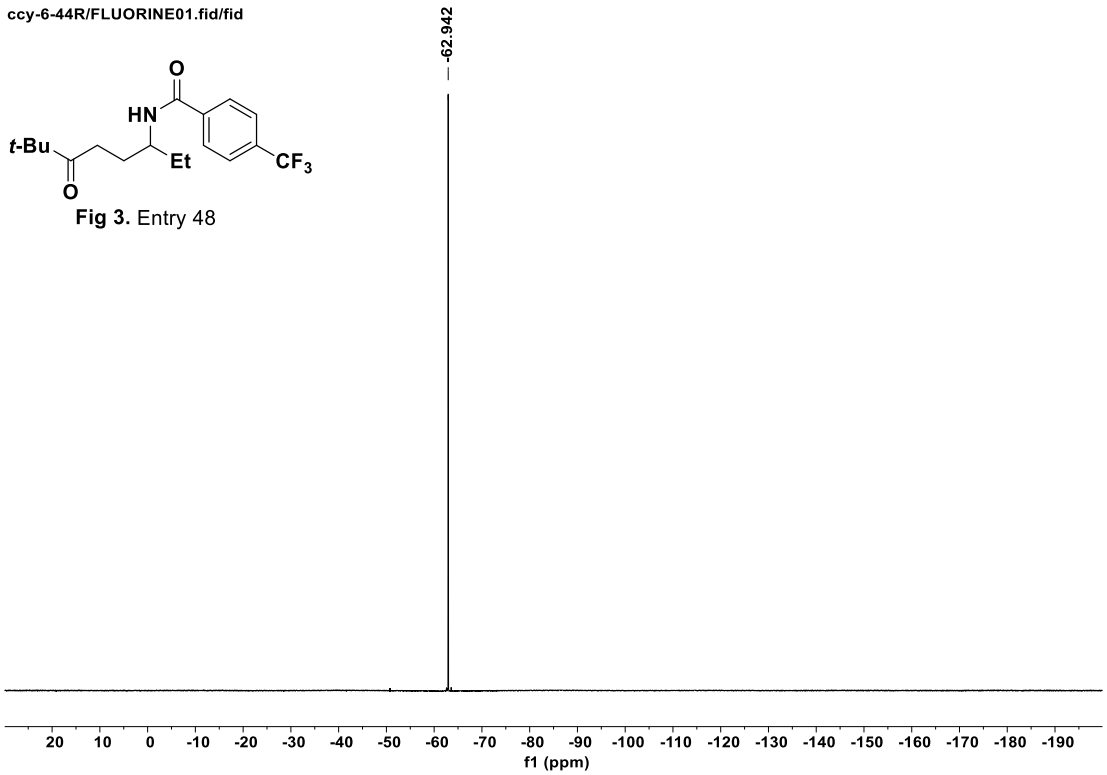

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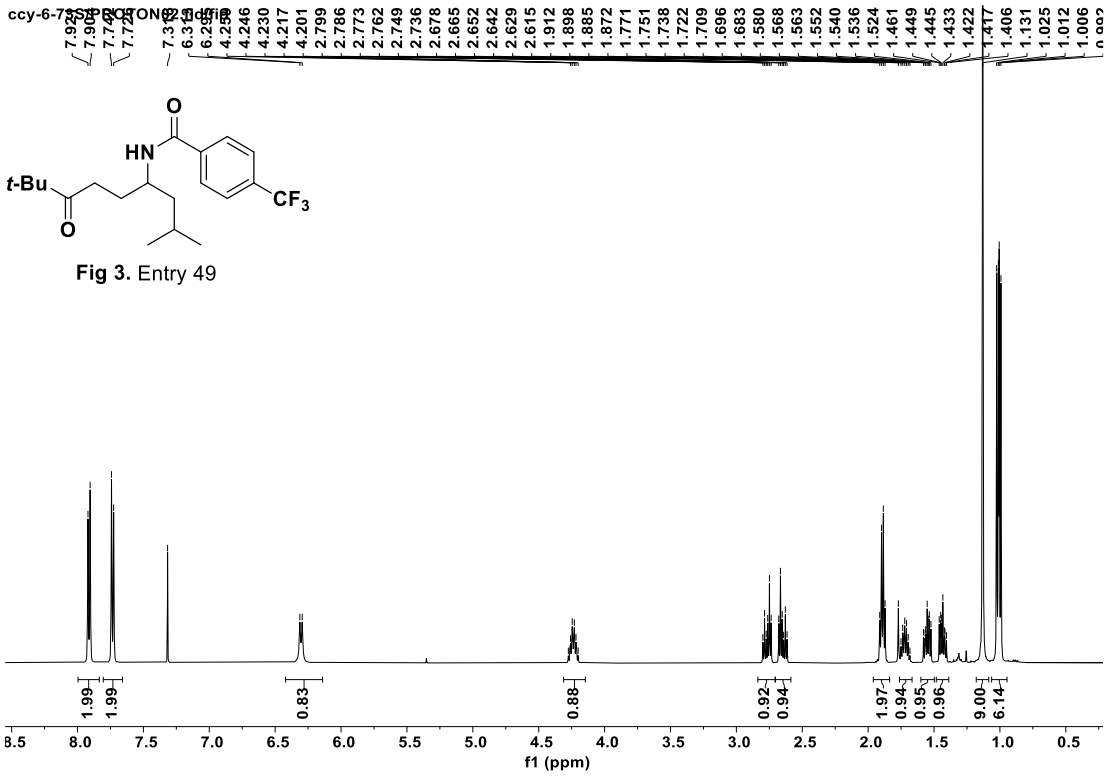

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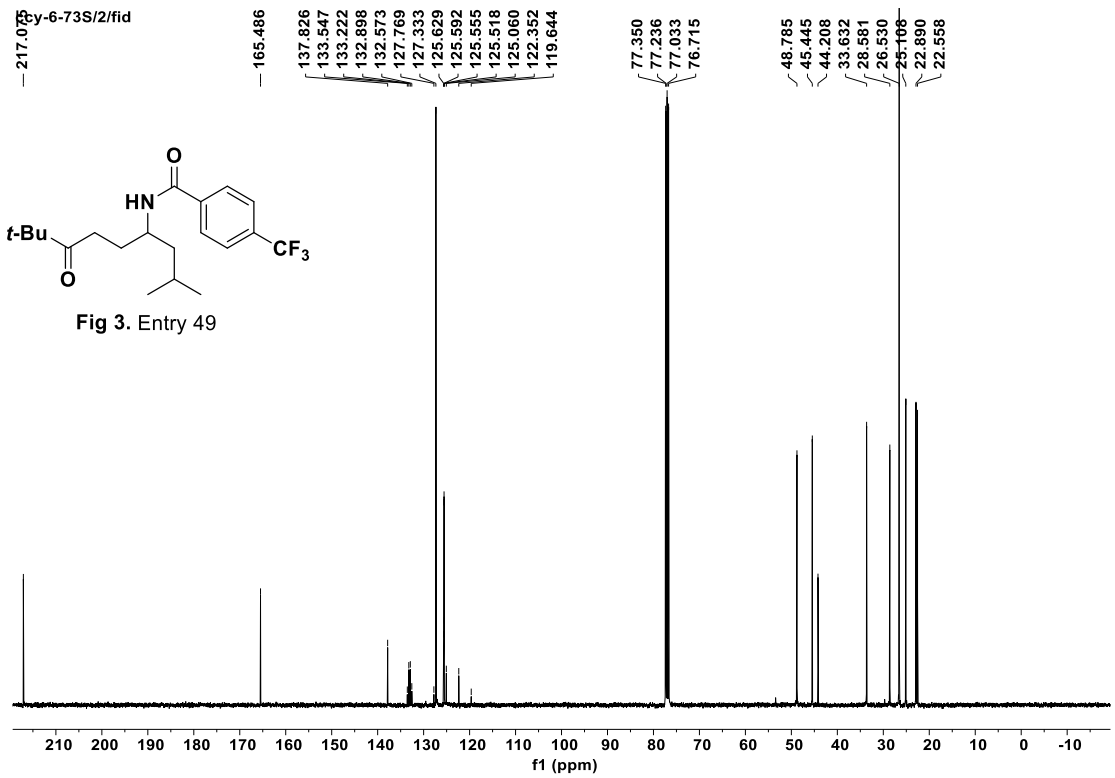

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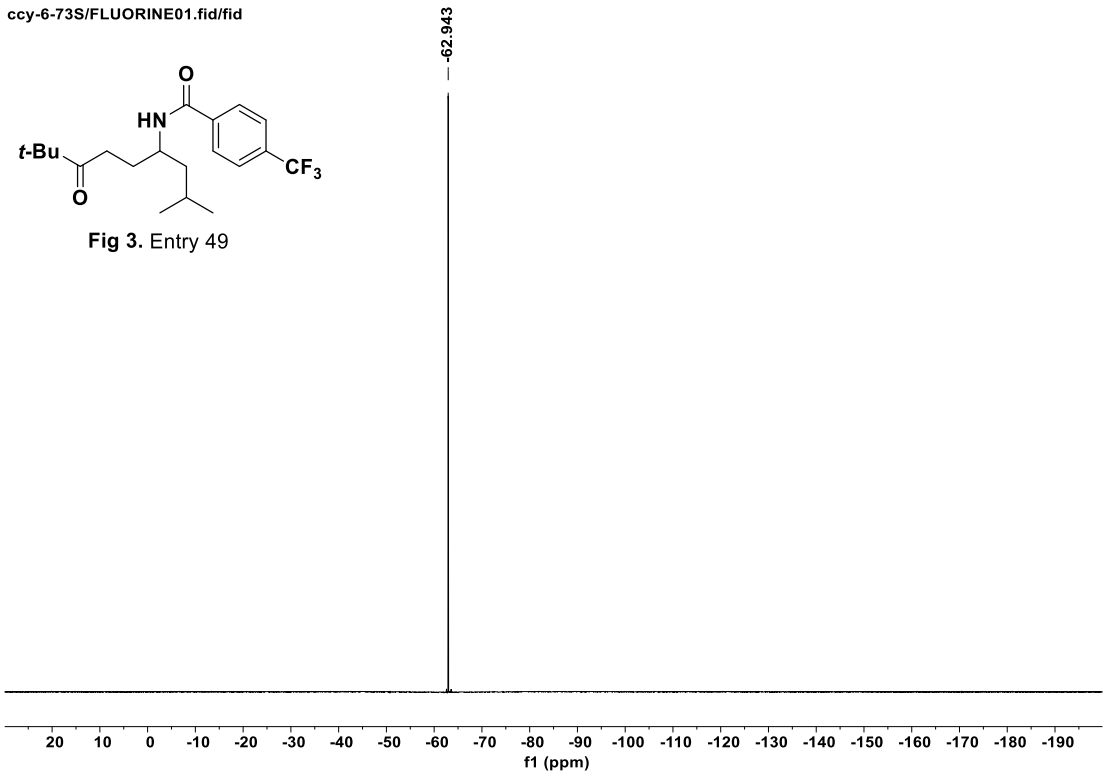

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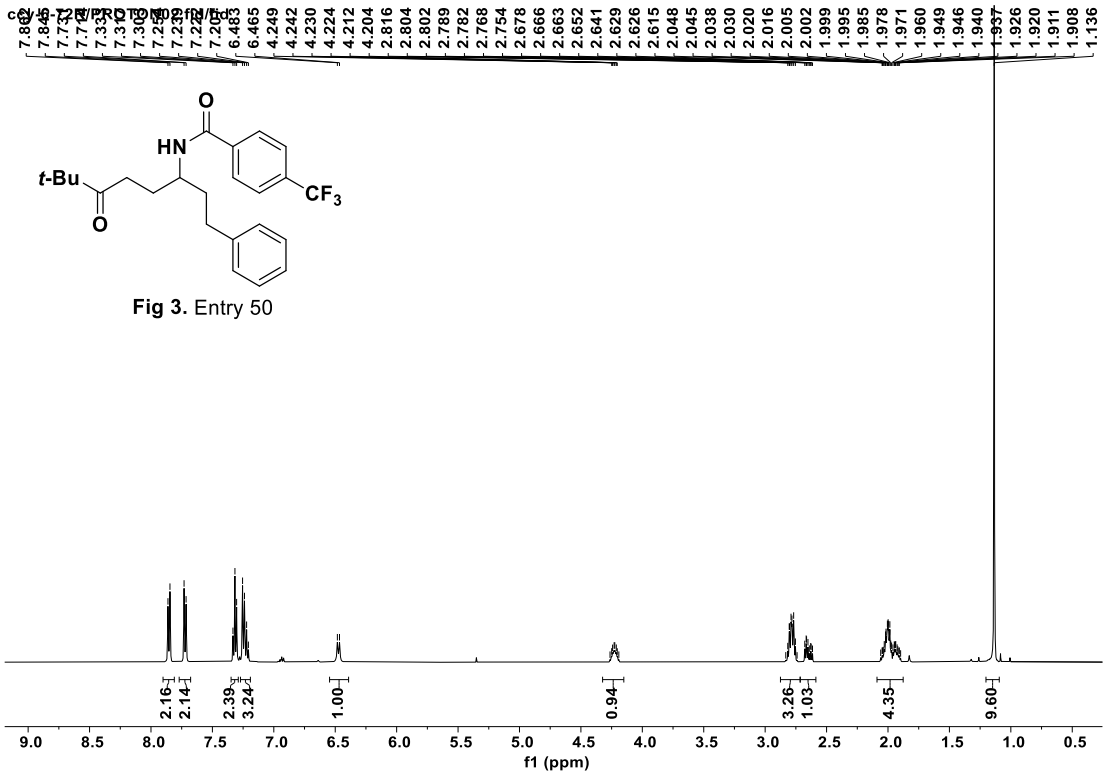

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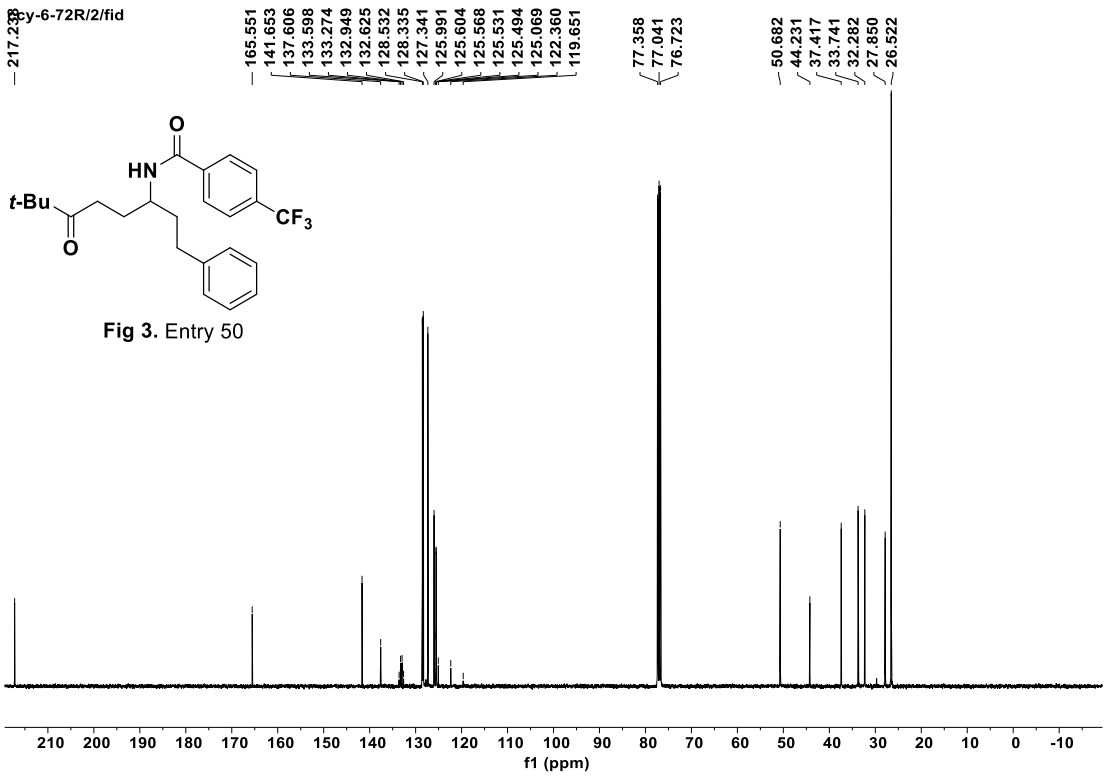

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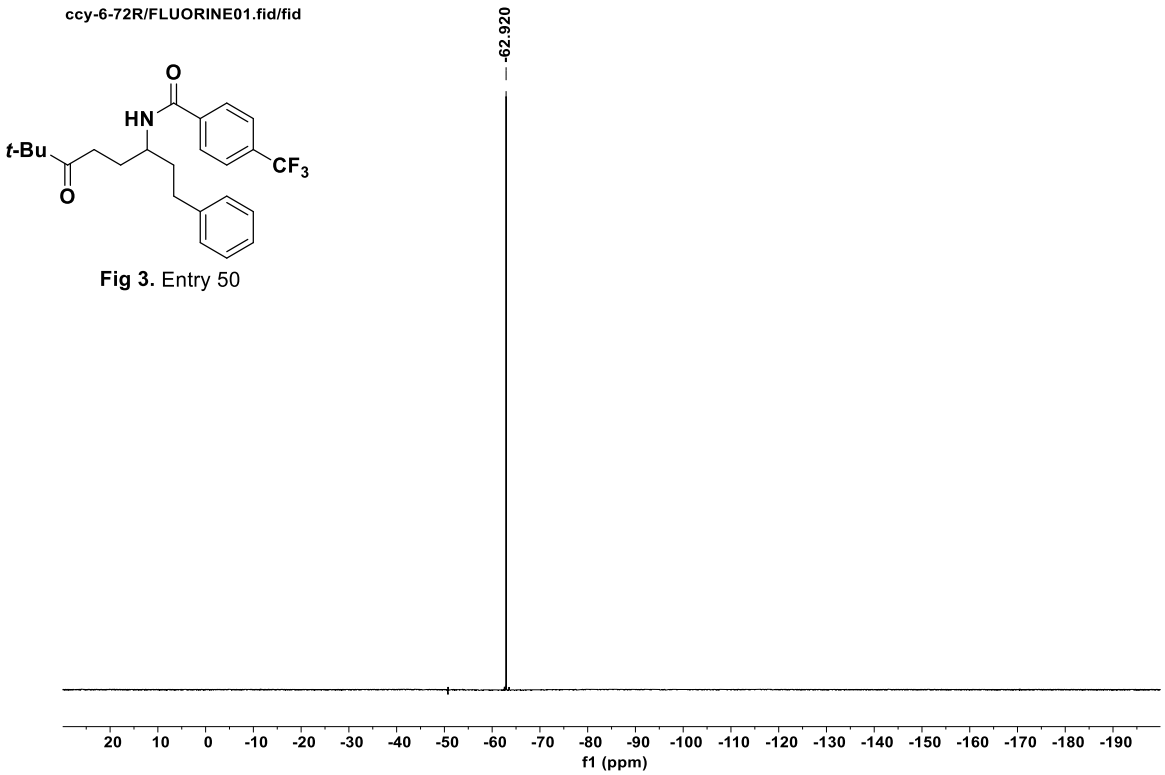

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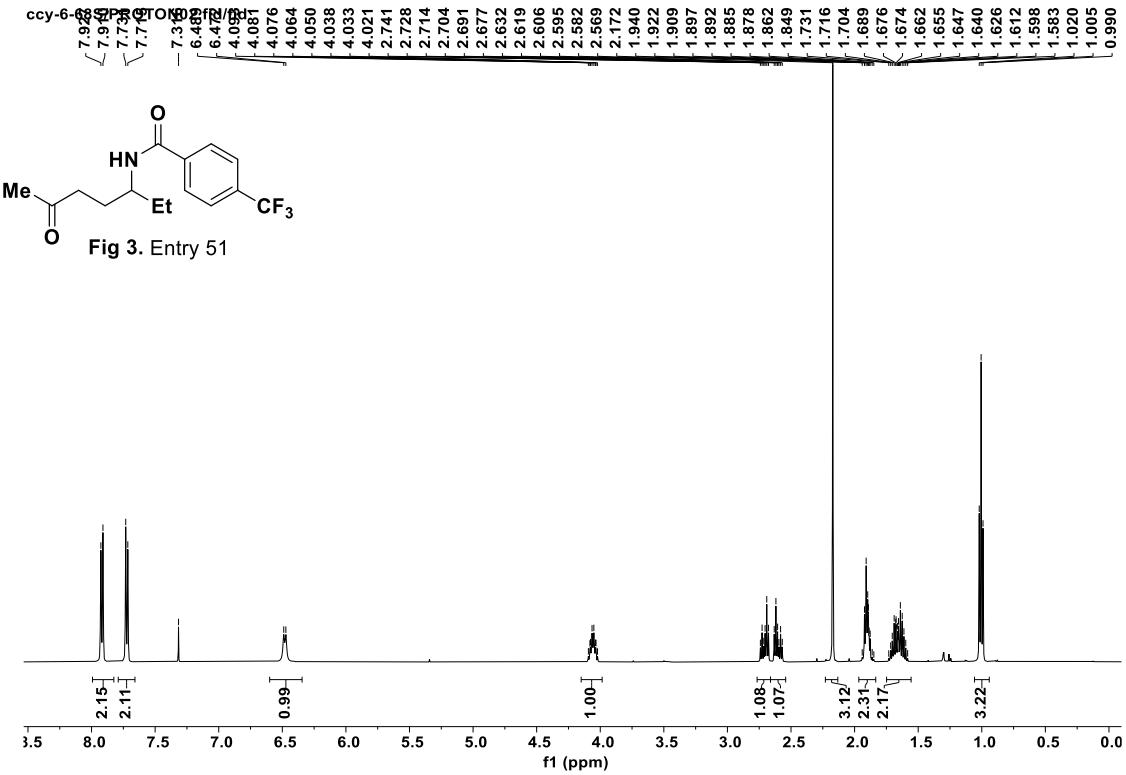

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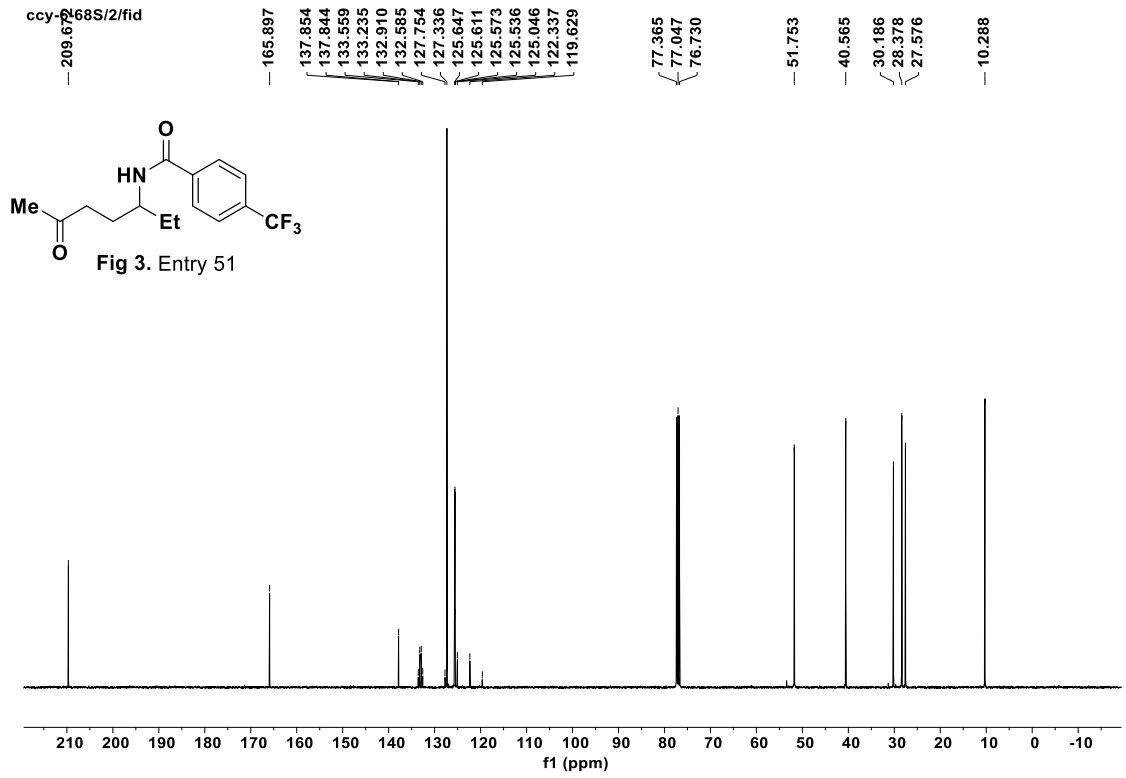

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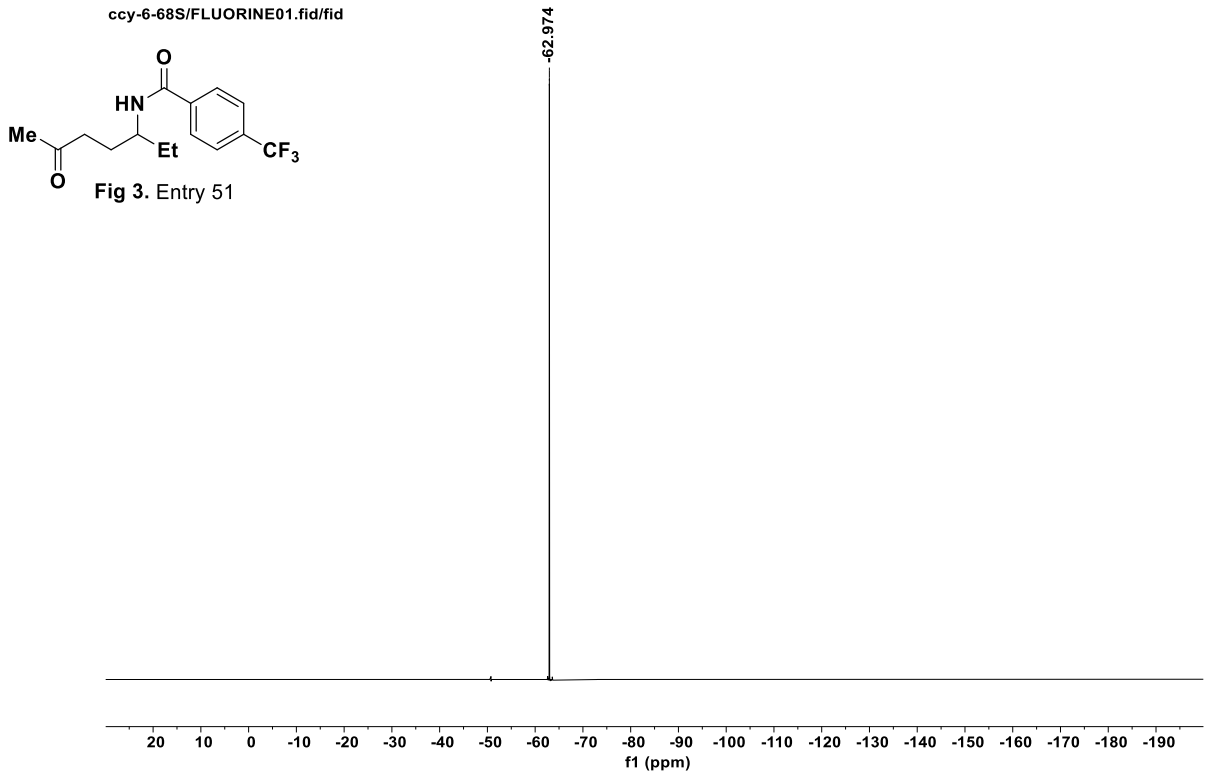

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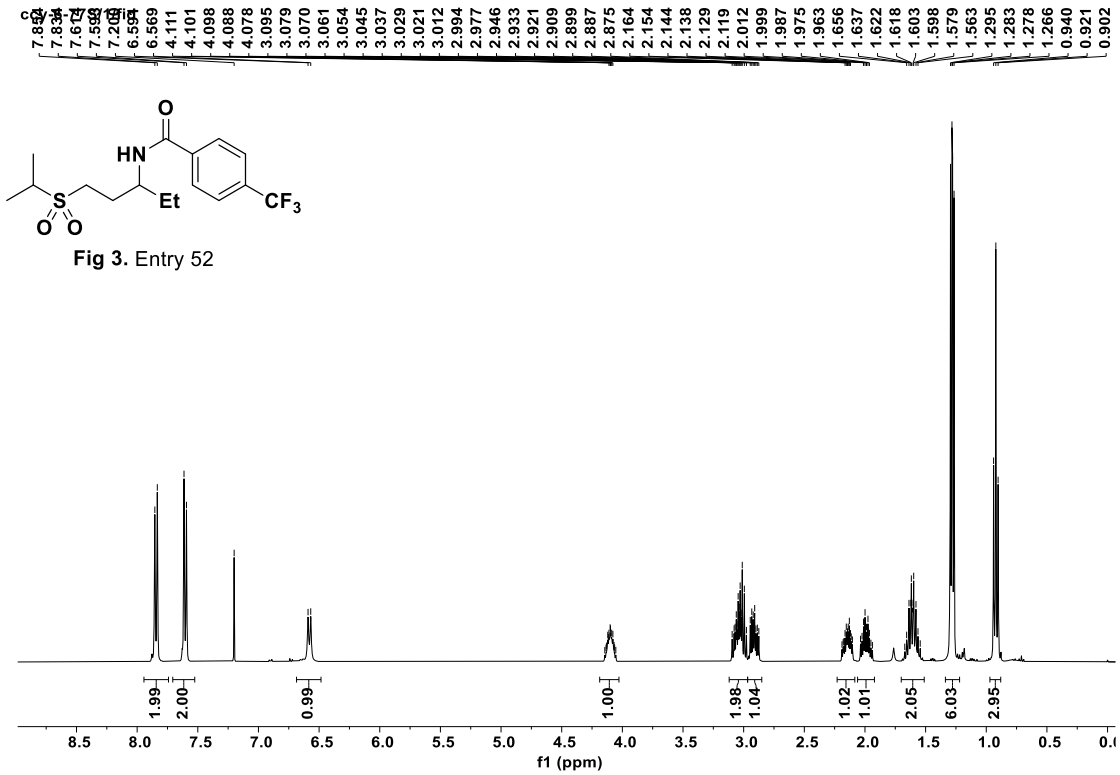

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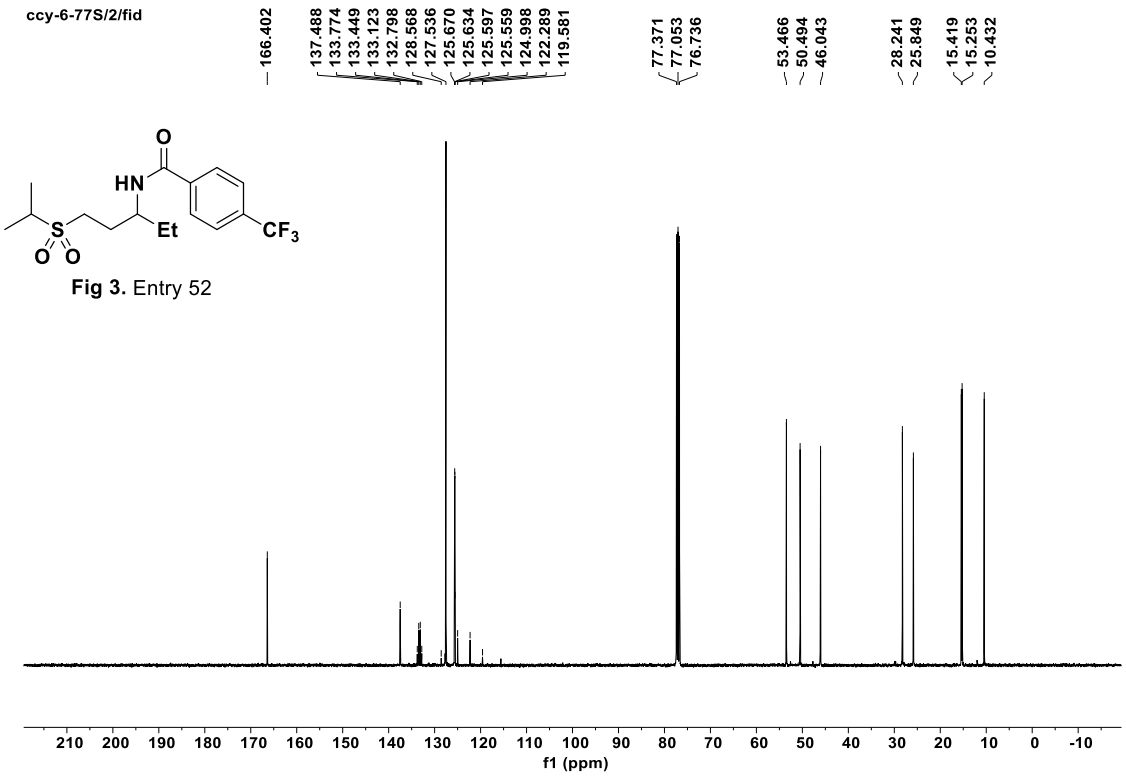

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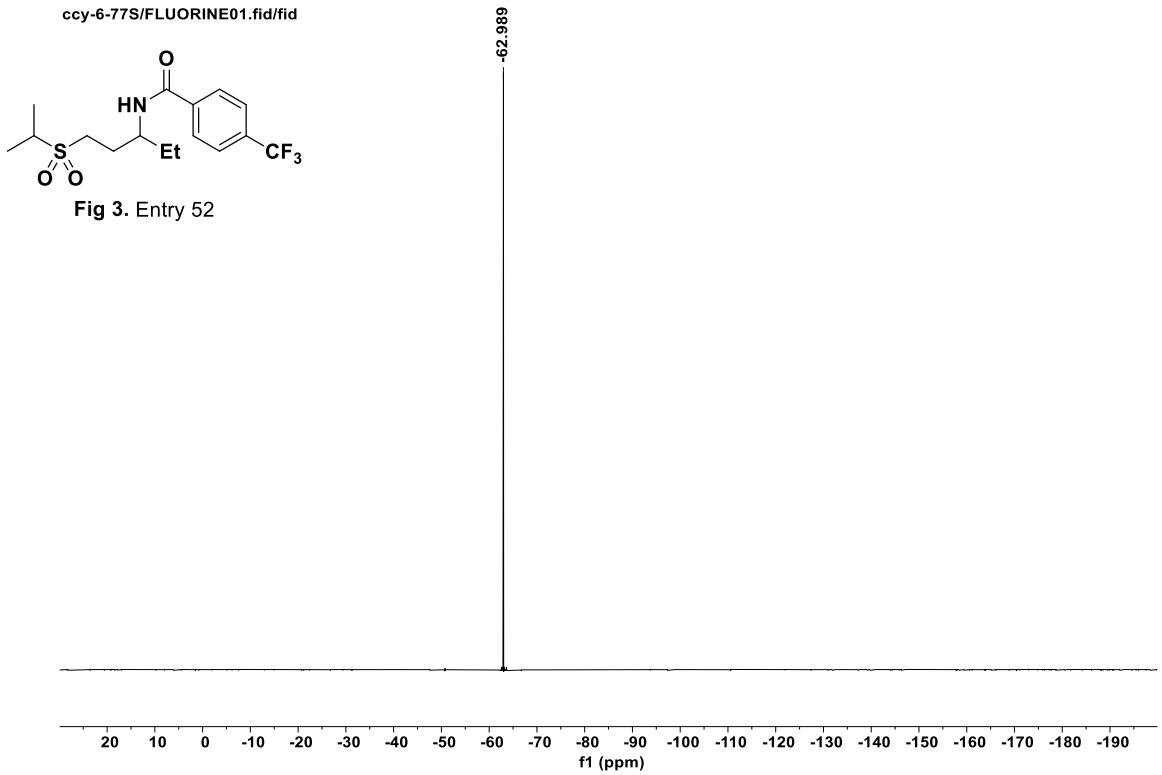

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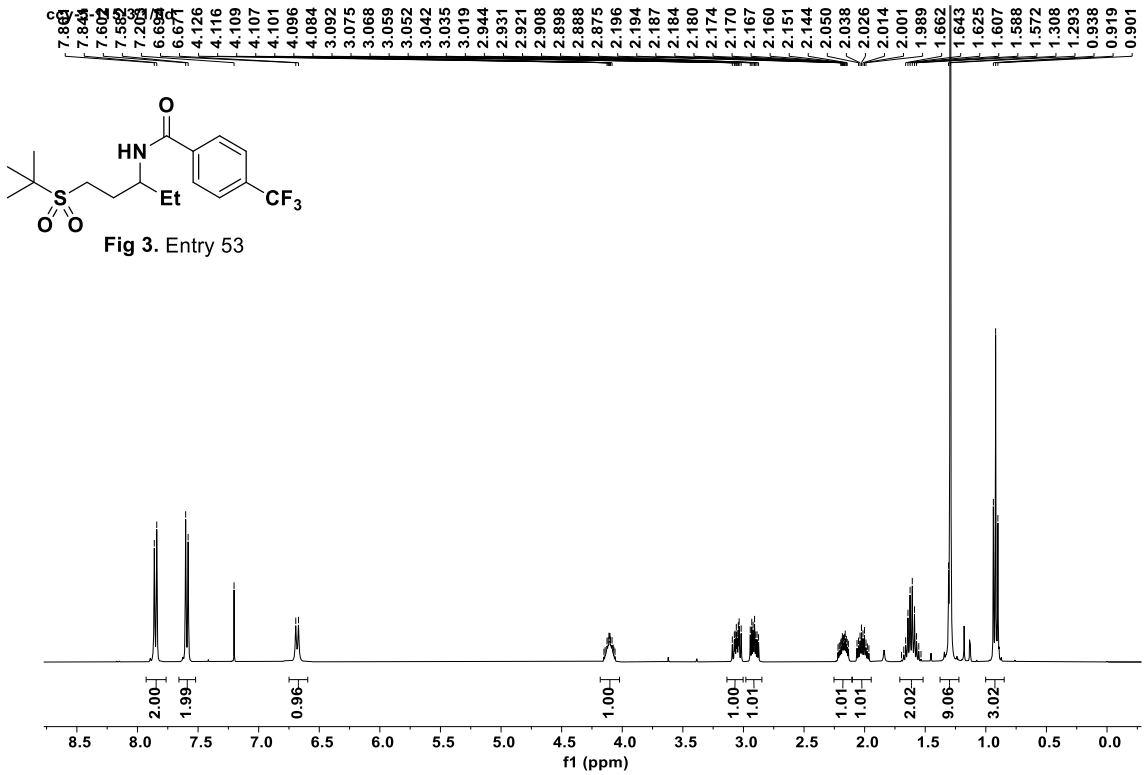

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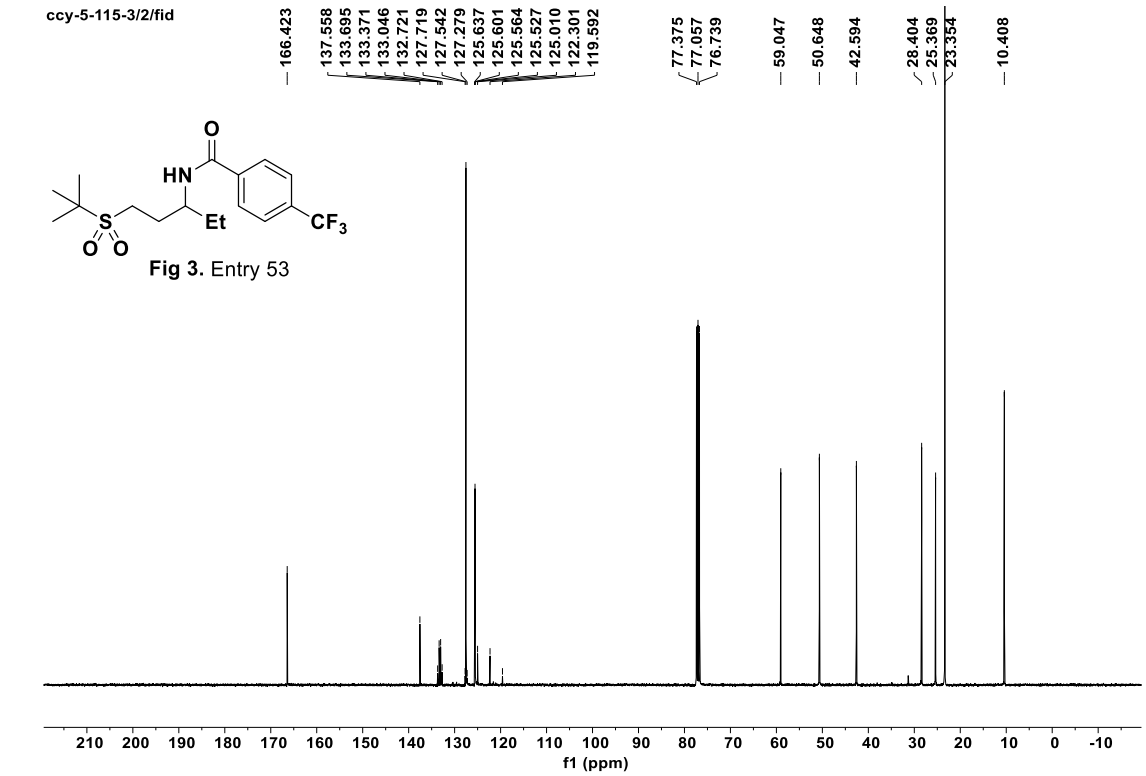

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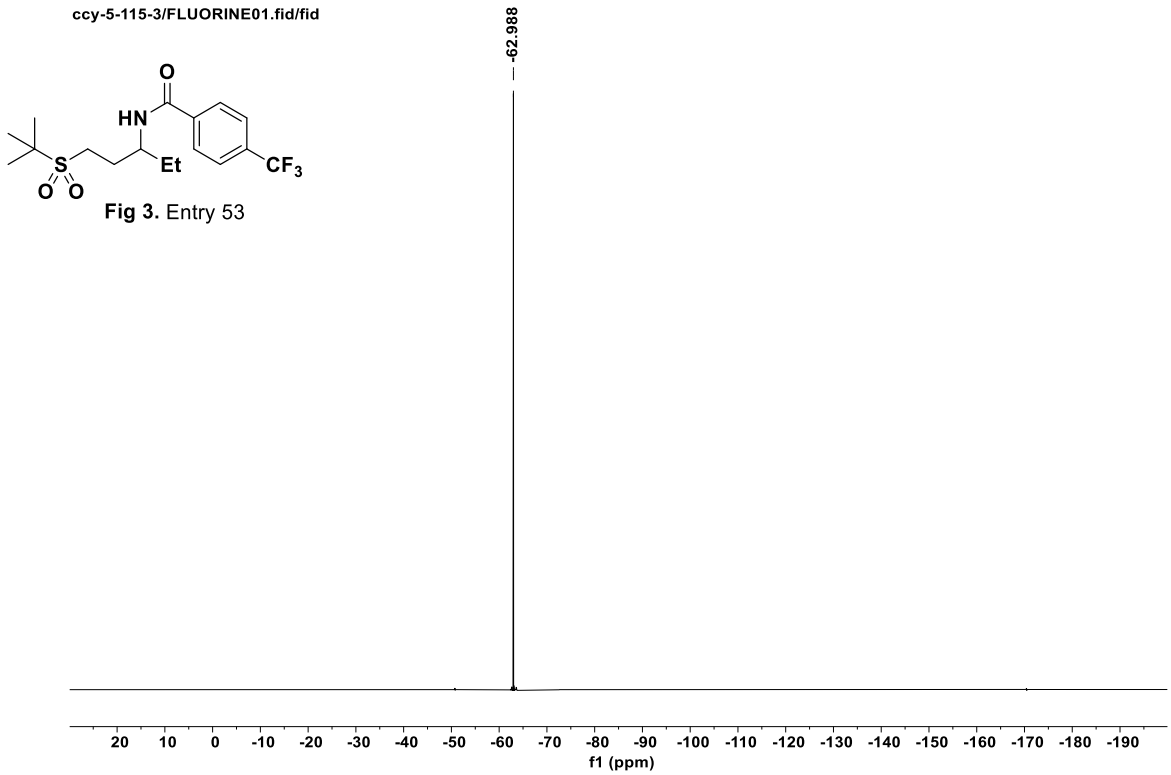

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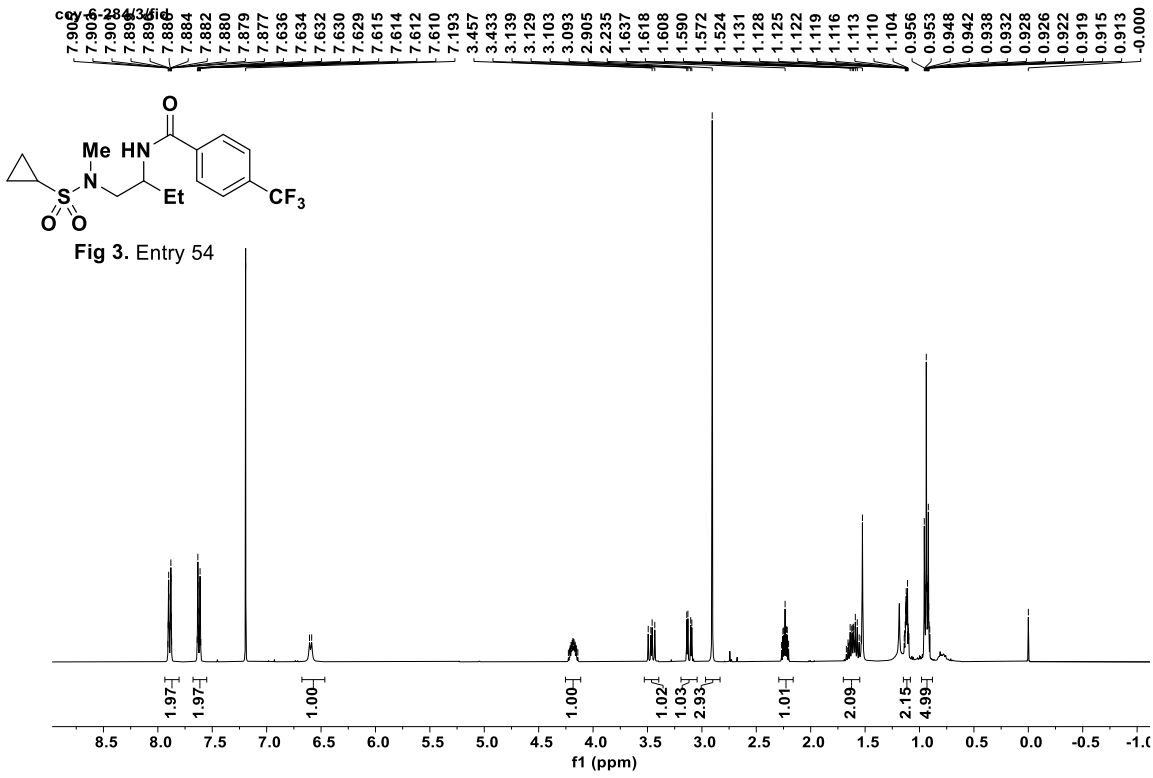

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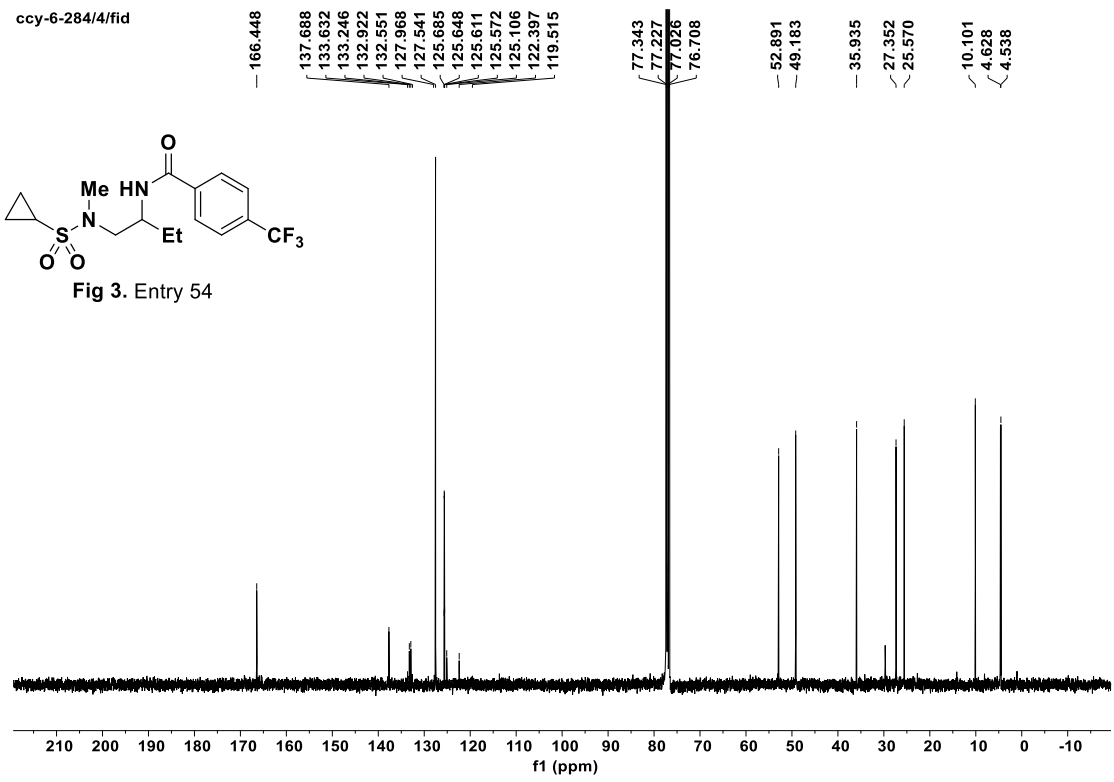


Fig 3. Entry 54

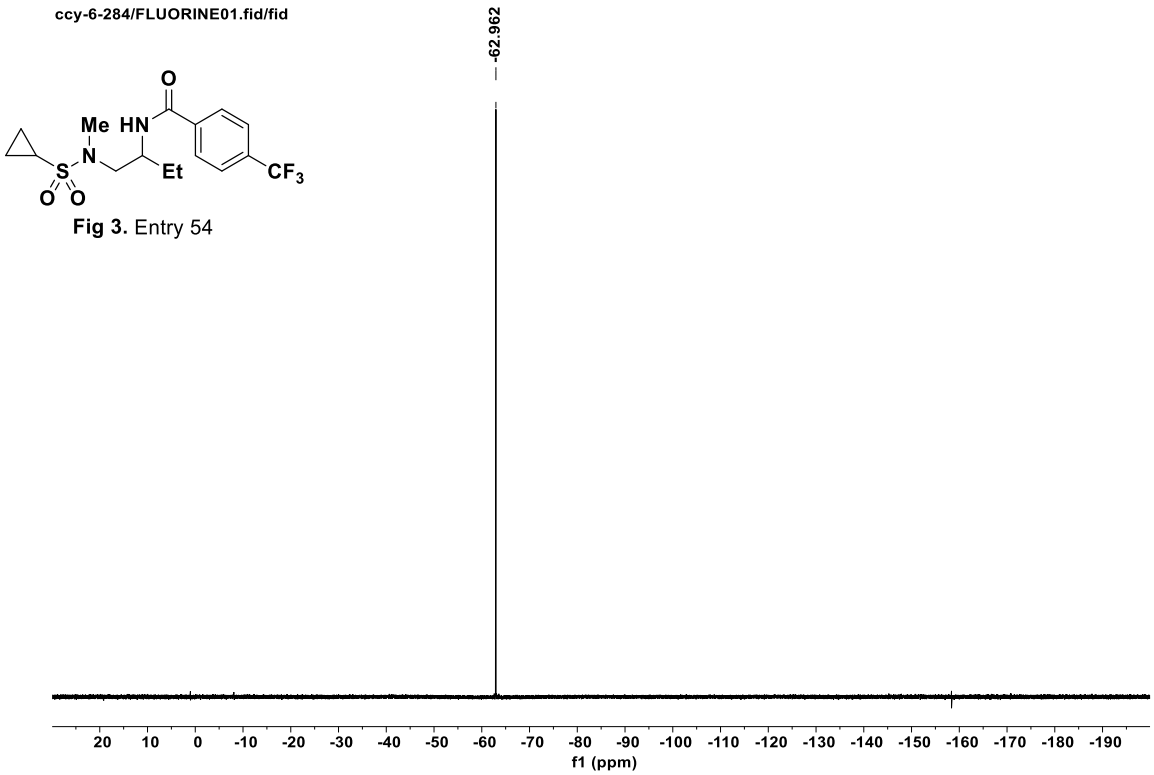
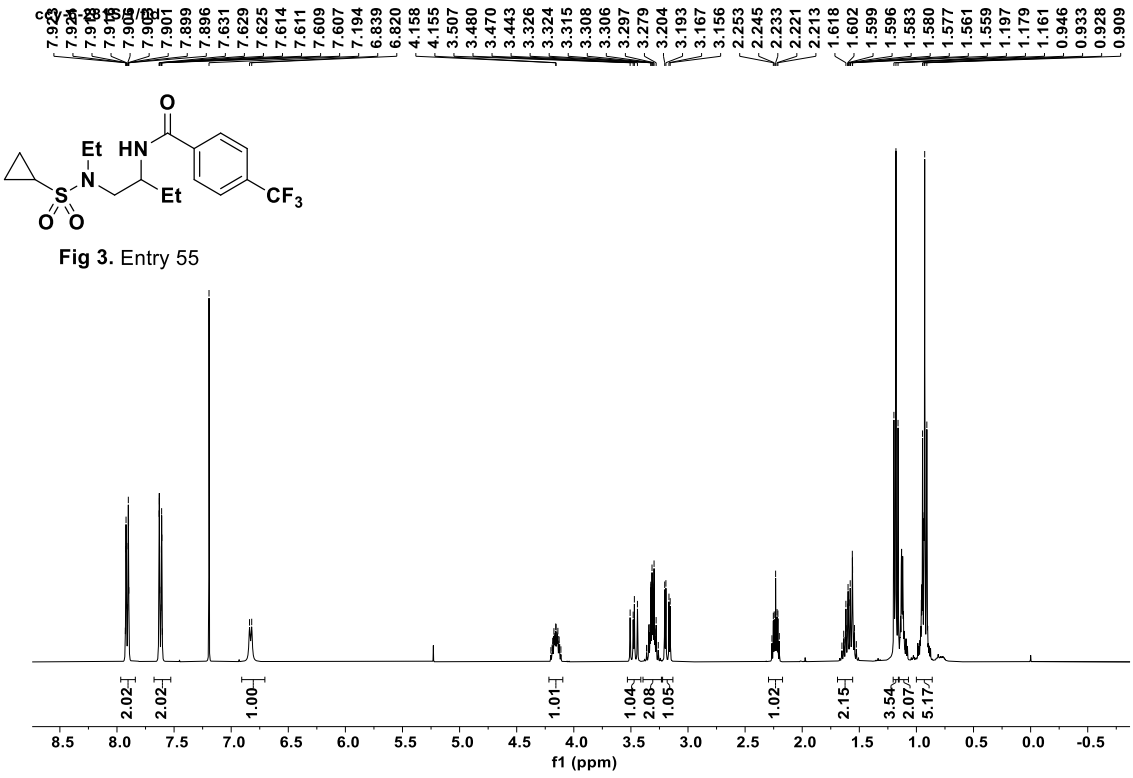


Fig 3. Entry 54



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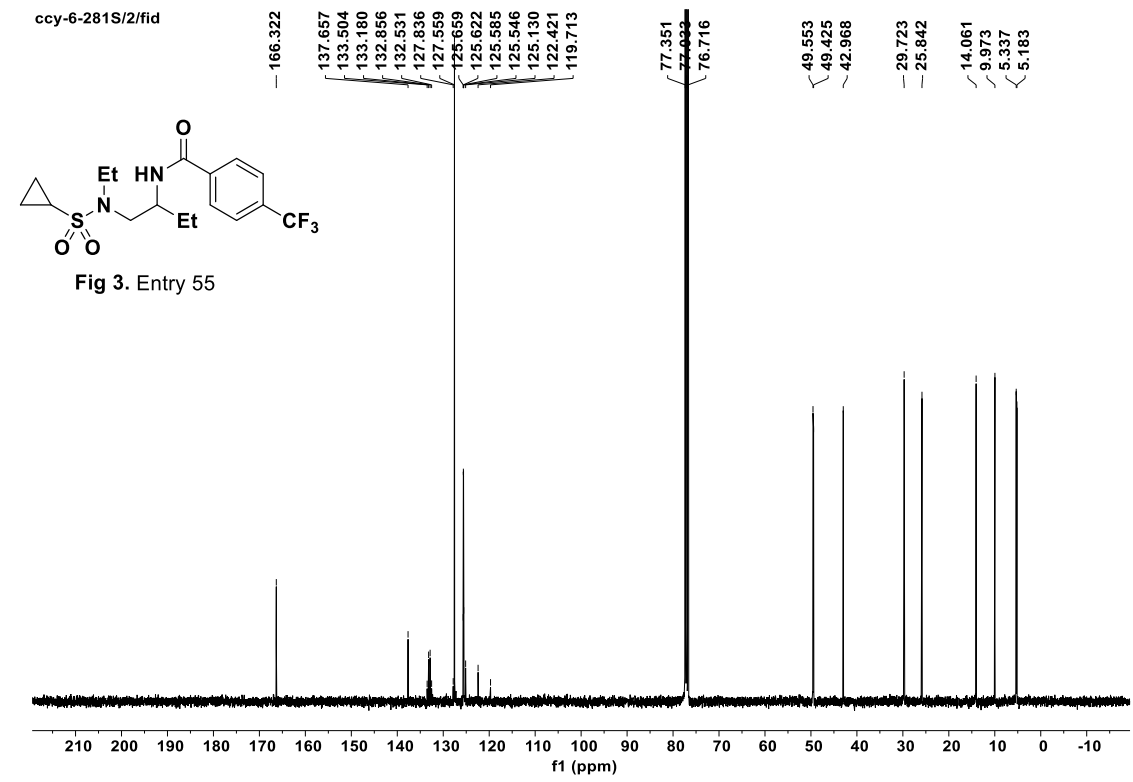

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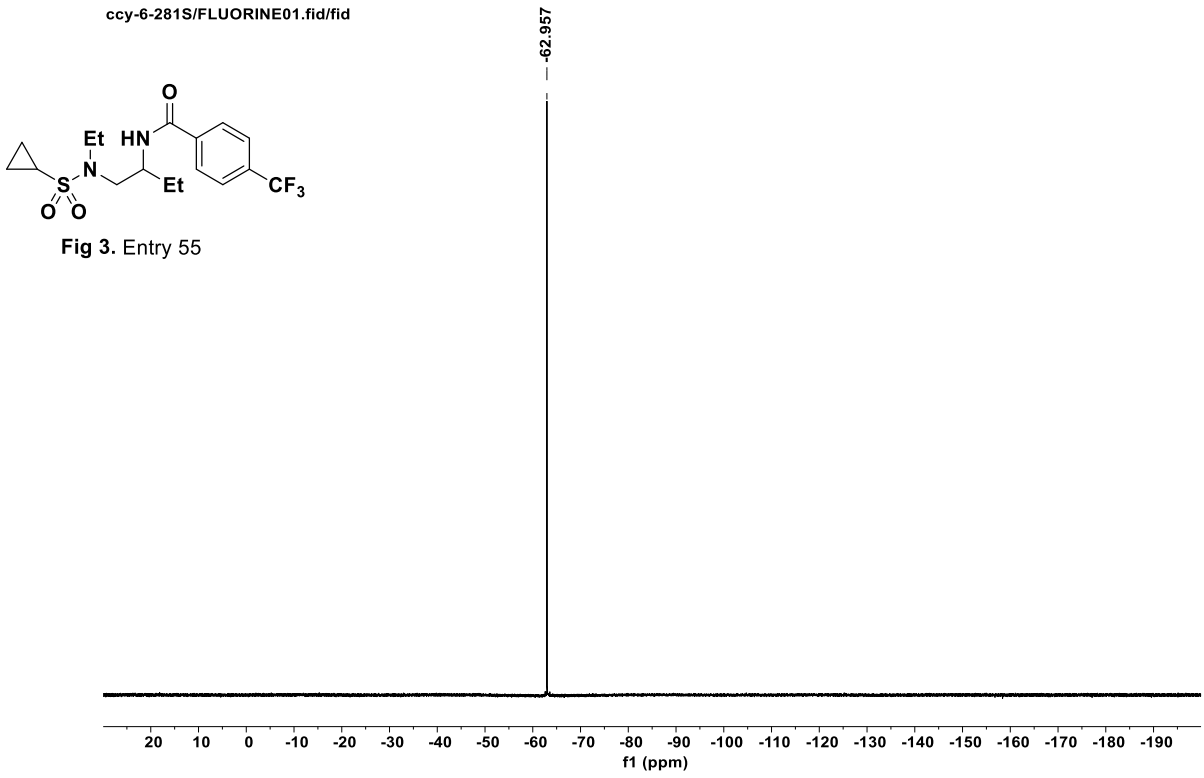

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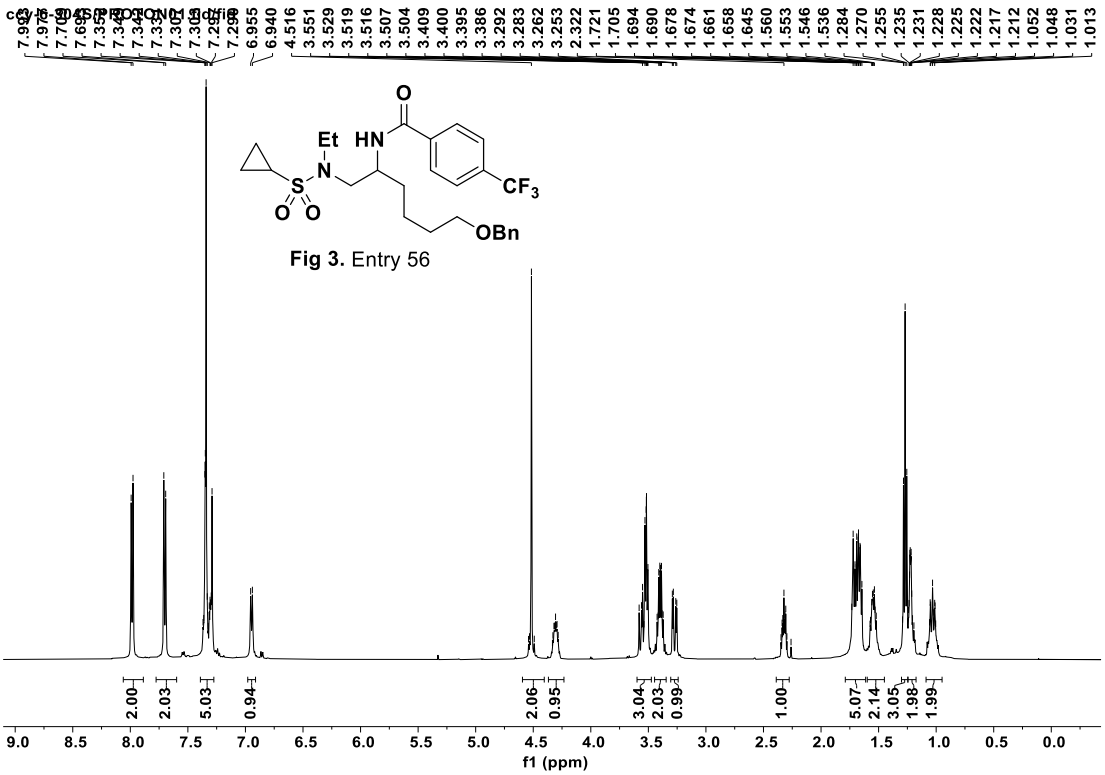

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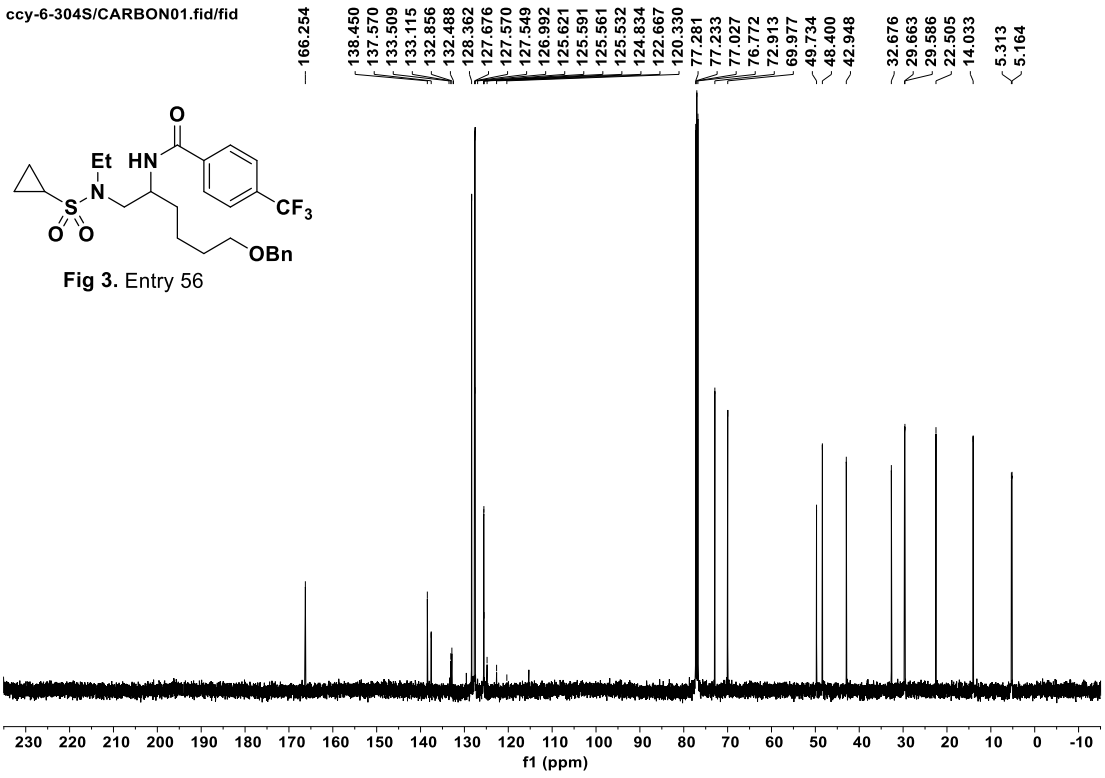

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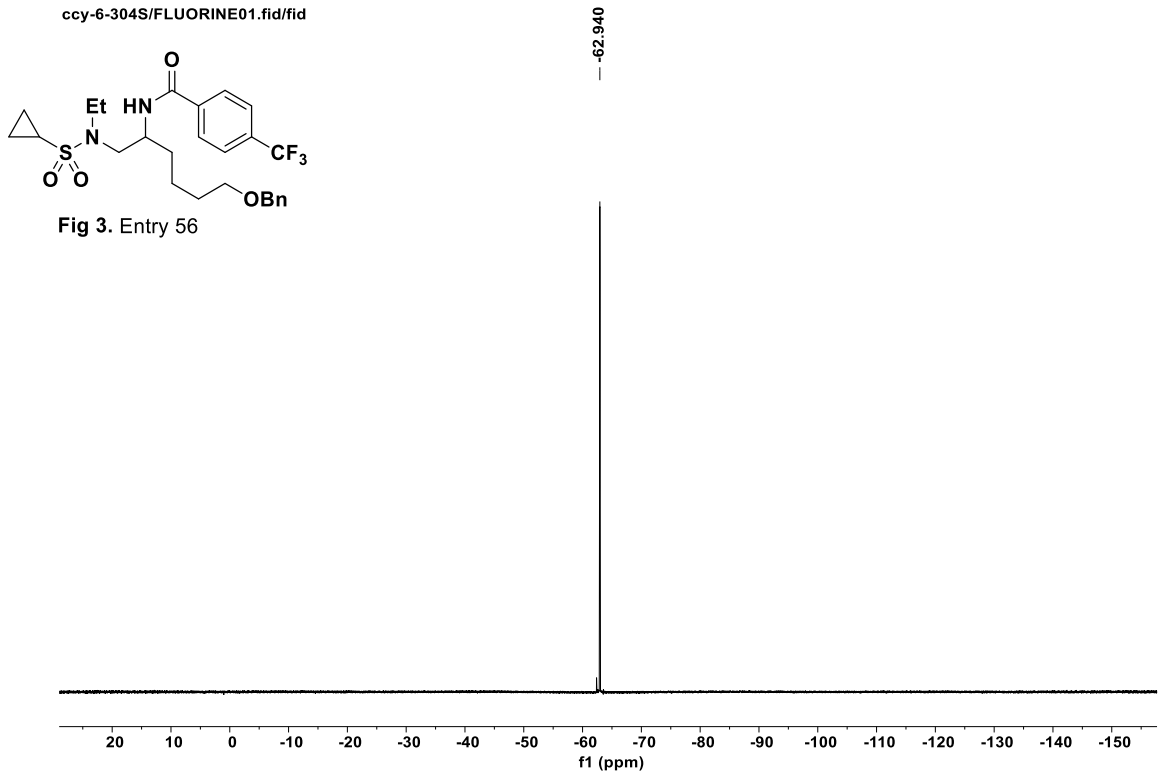

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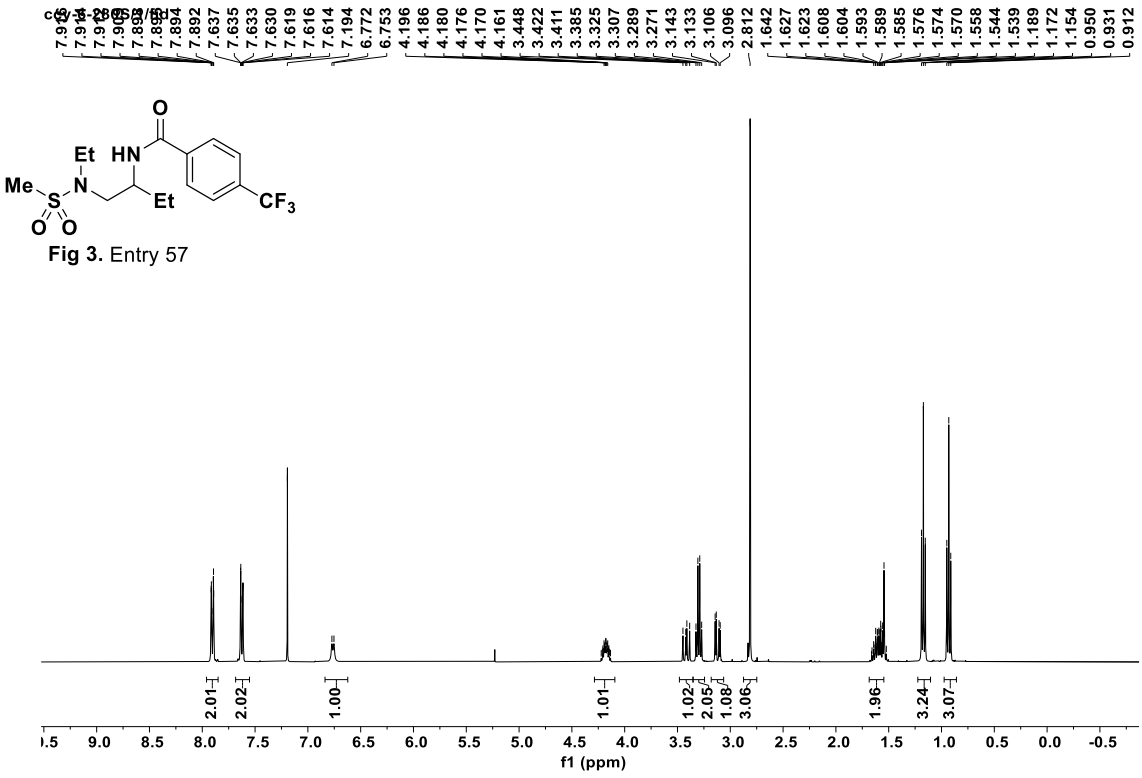

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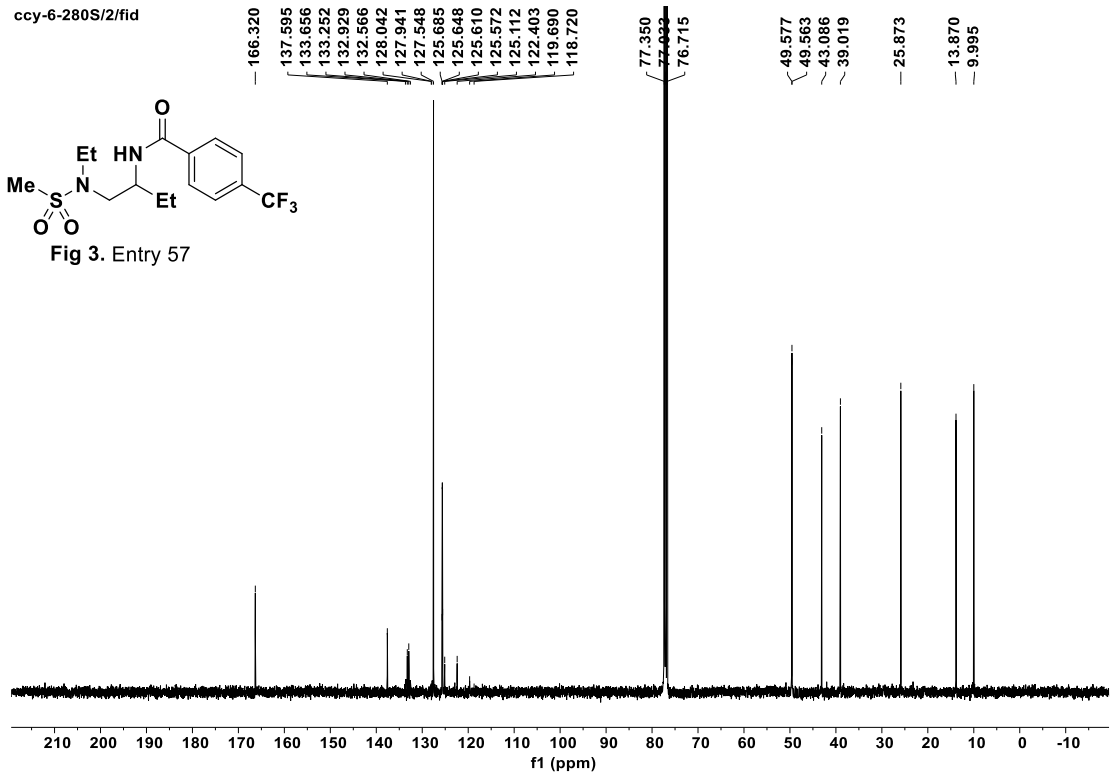

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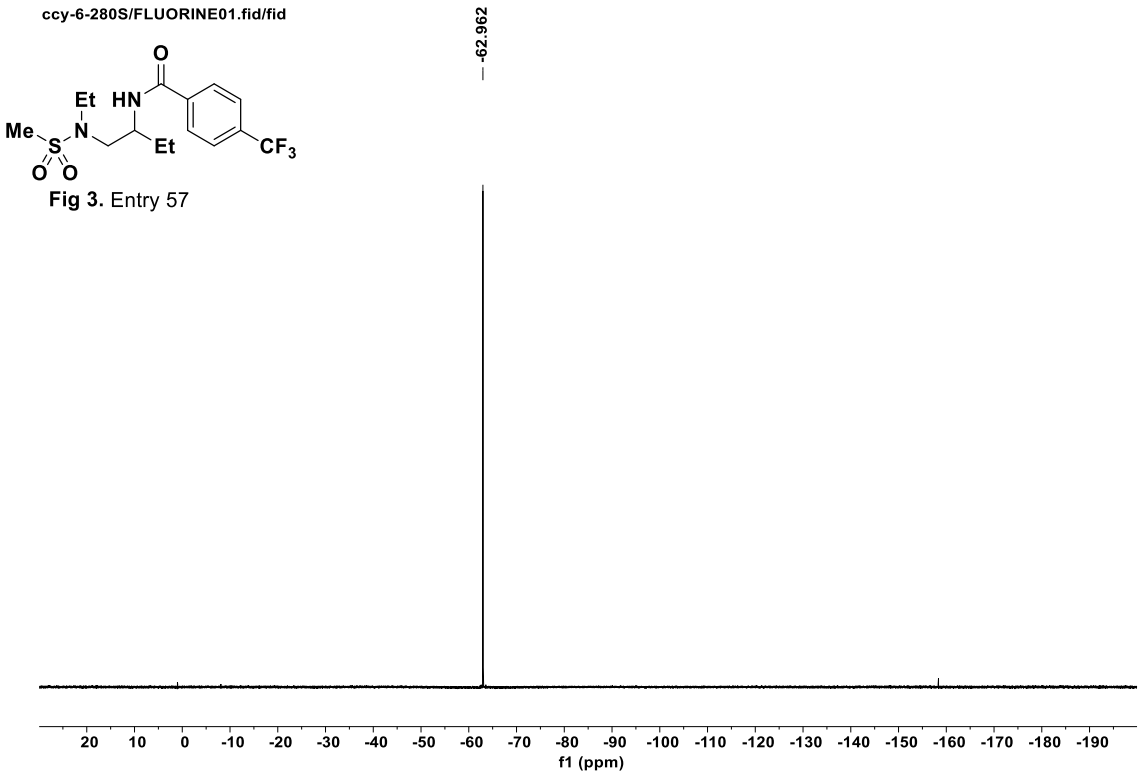

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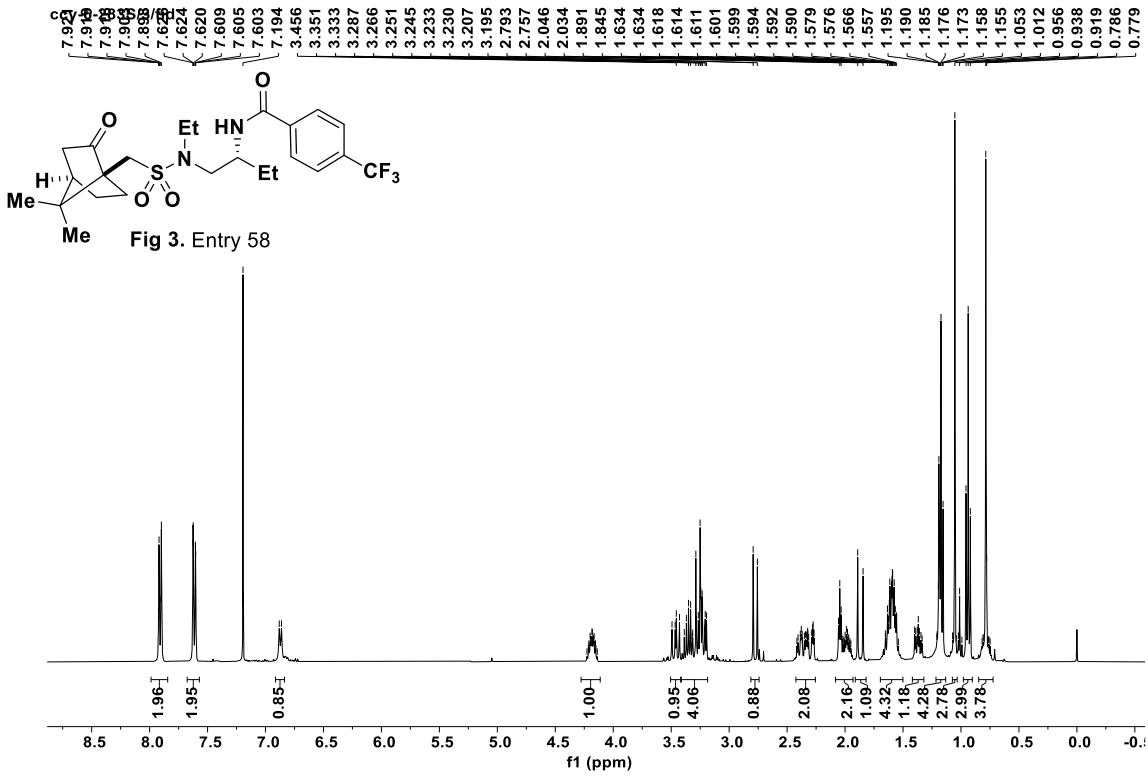

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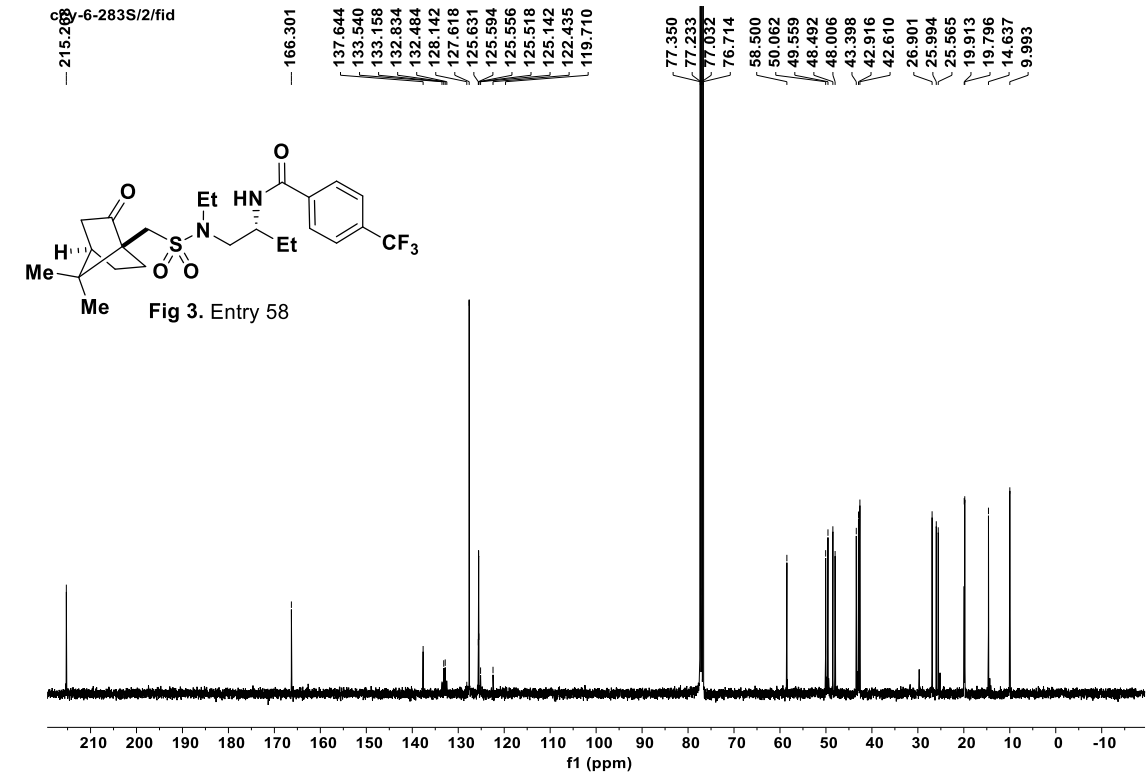

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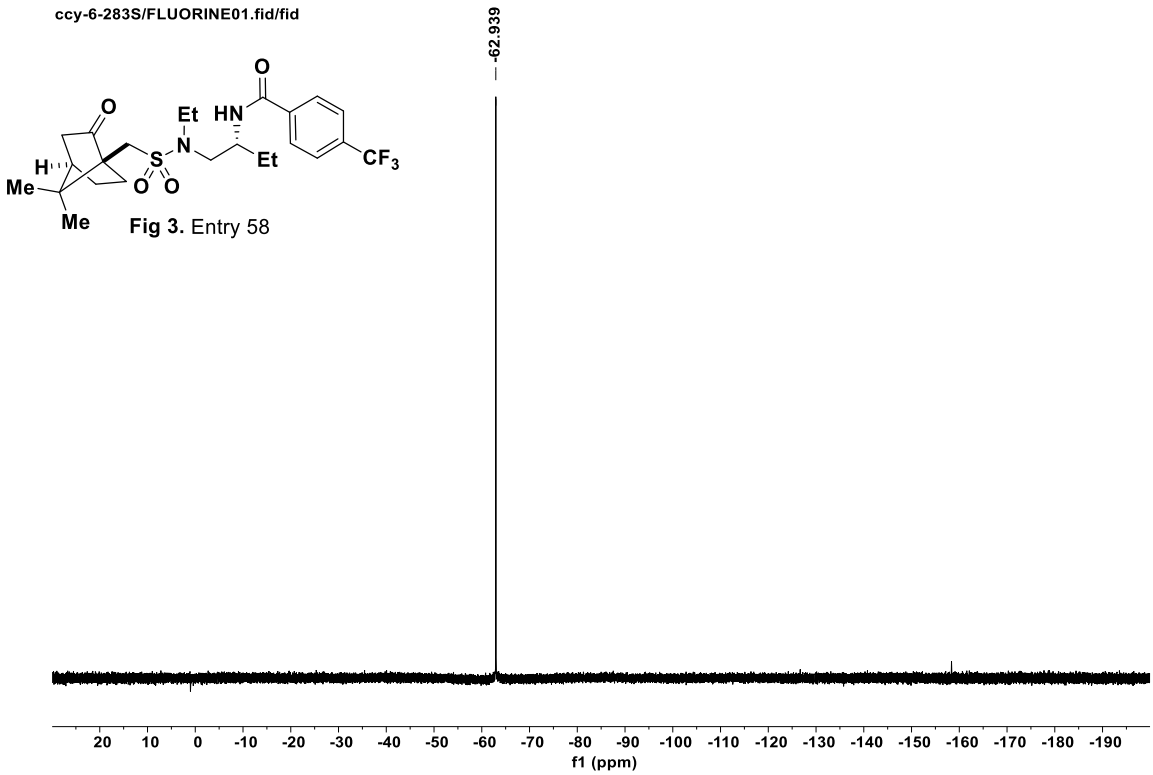

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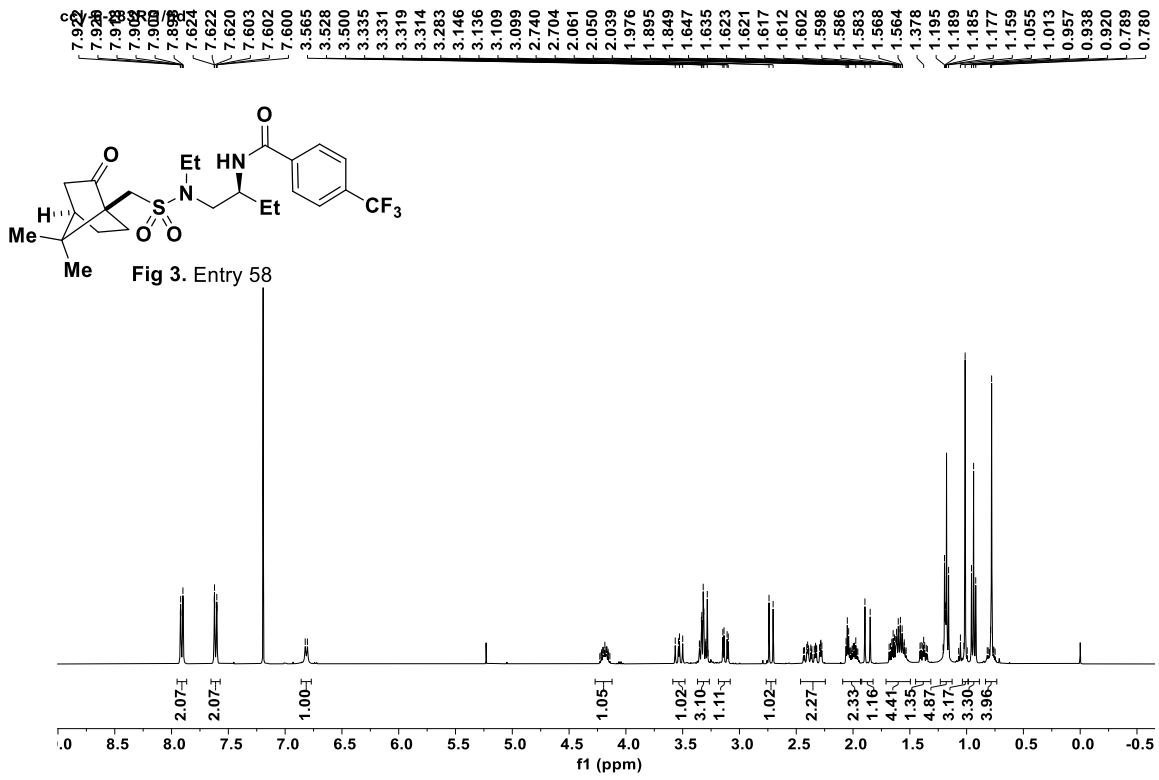

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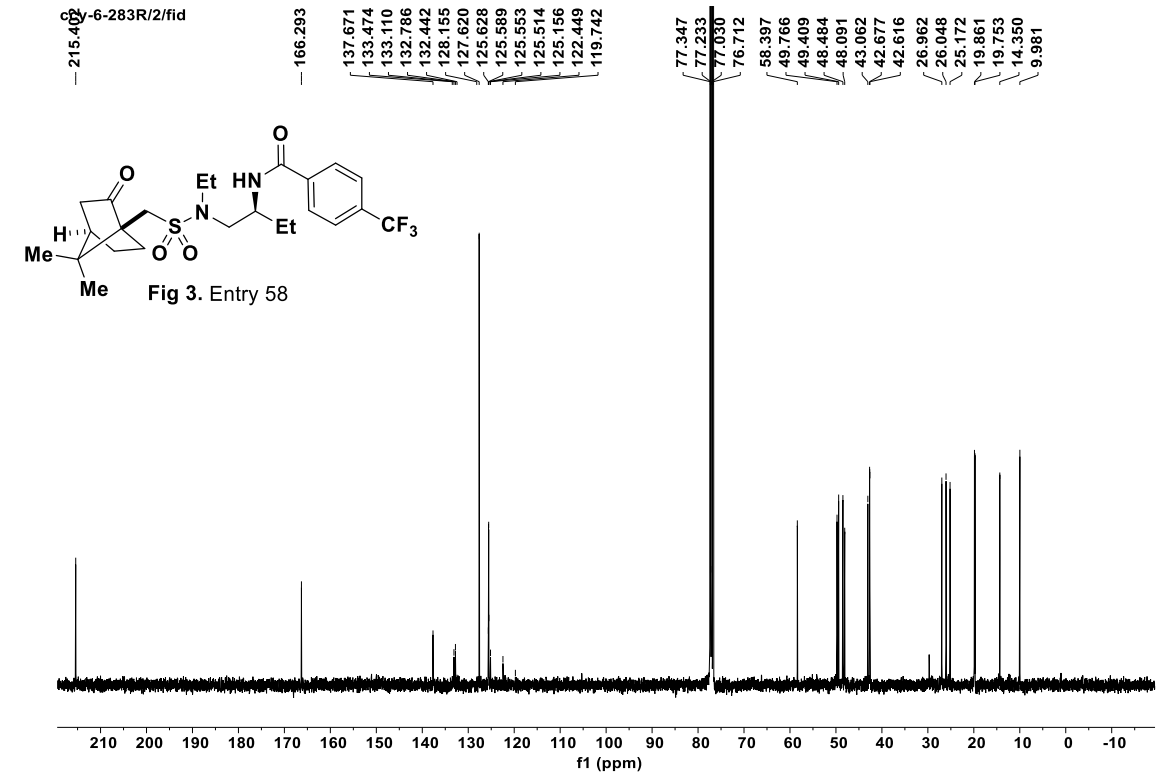

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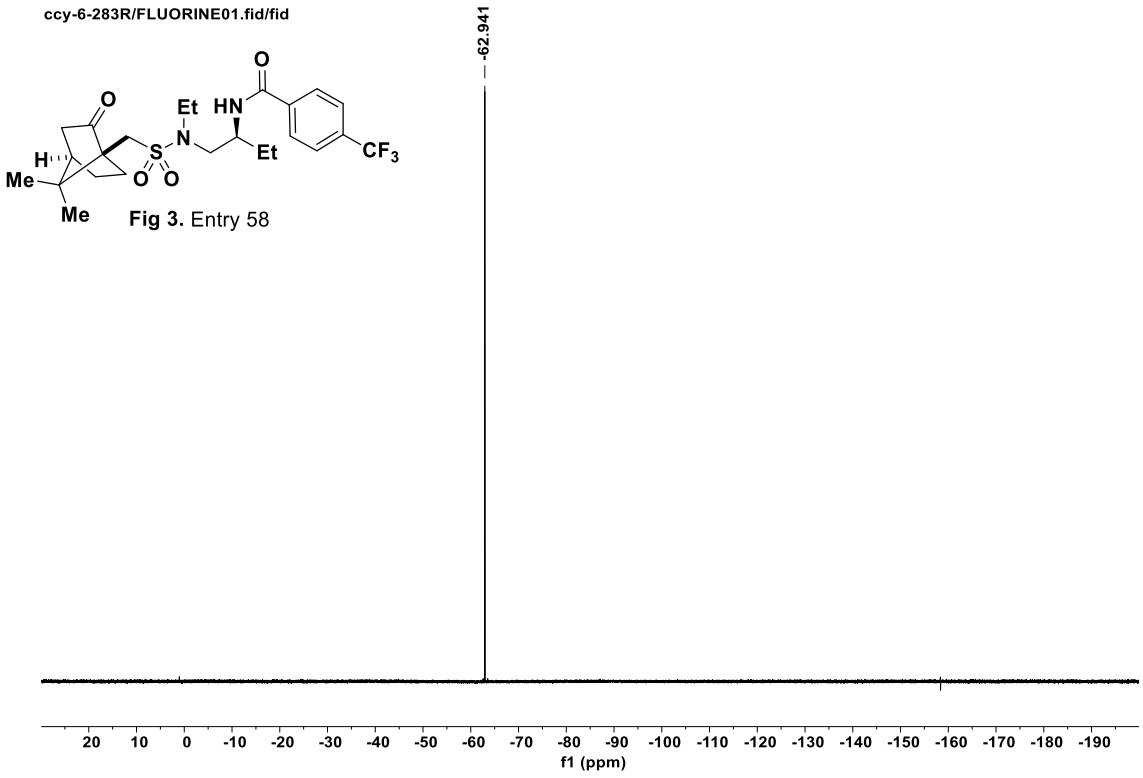

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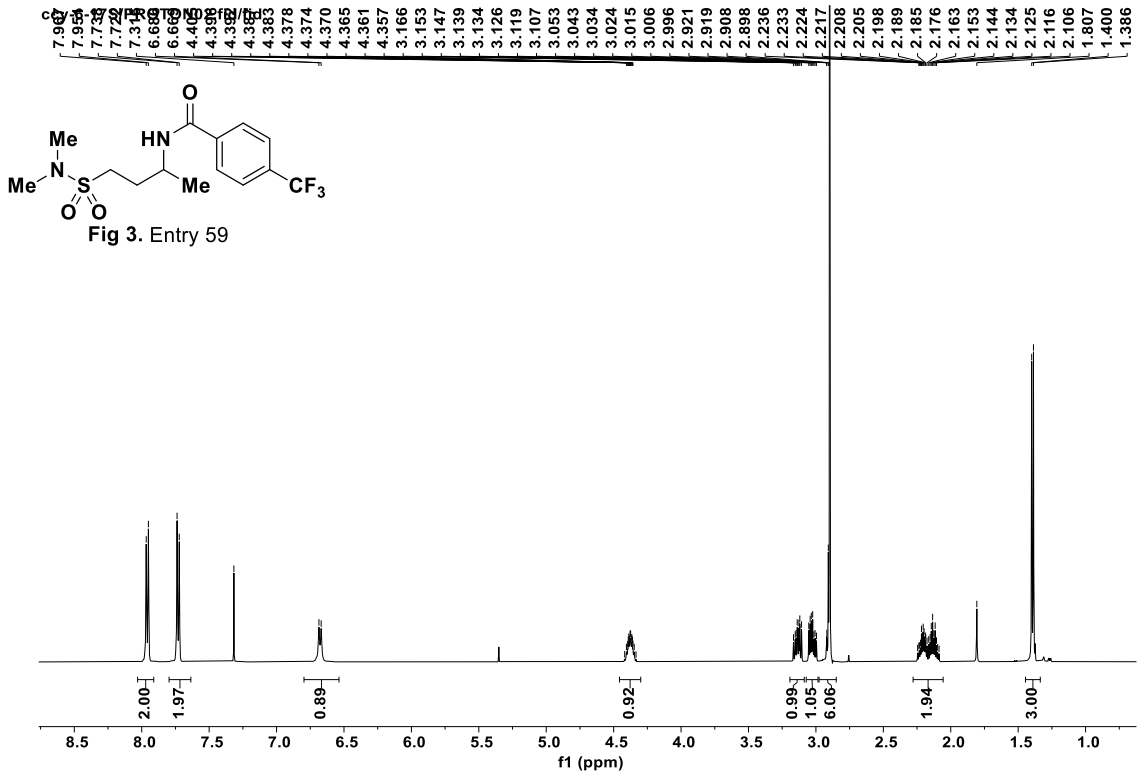


Fig 3. Entry 59

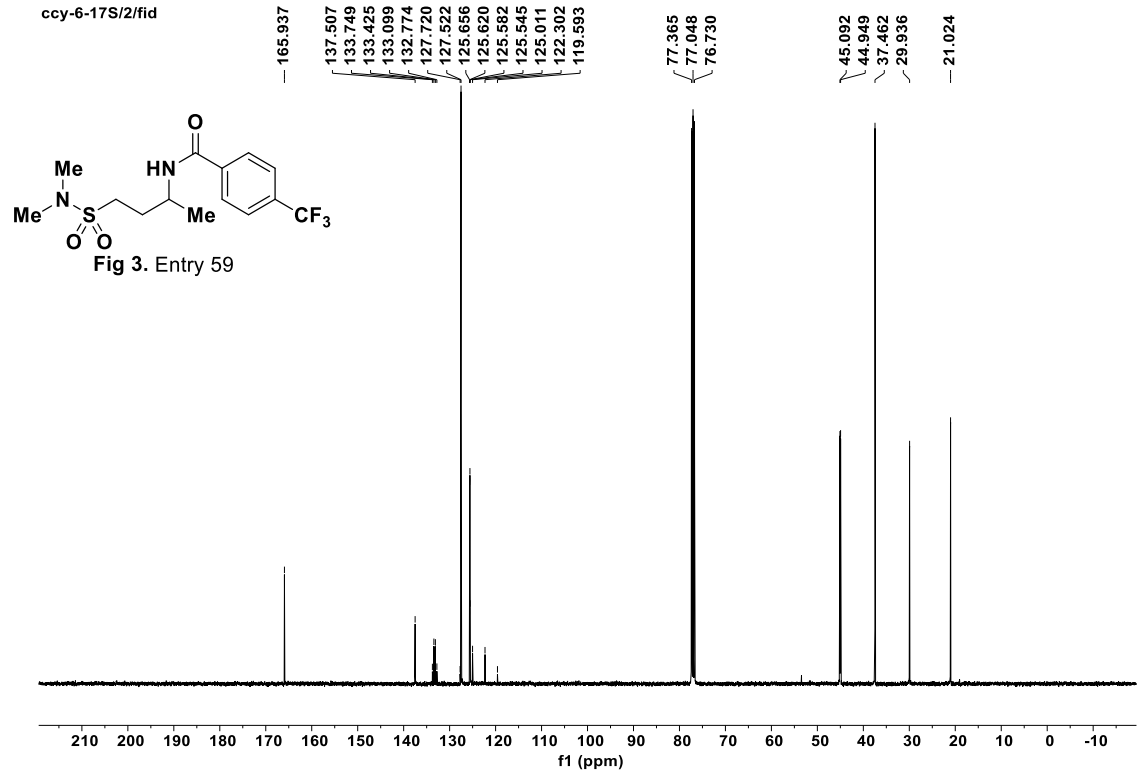
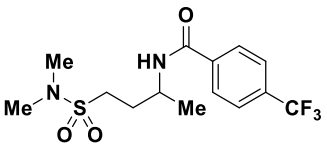


Fig 3. Entry 59

ccy-6-17S/FLUORINE01.fid/fid



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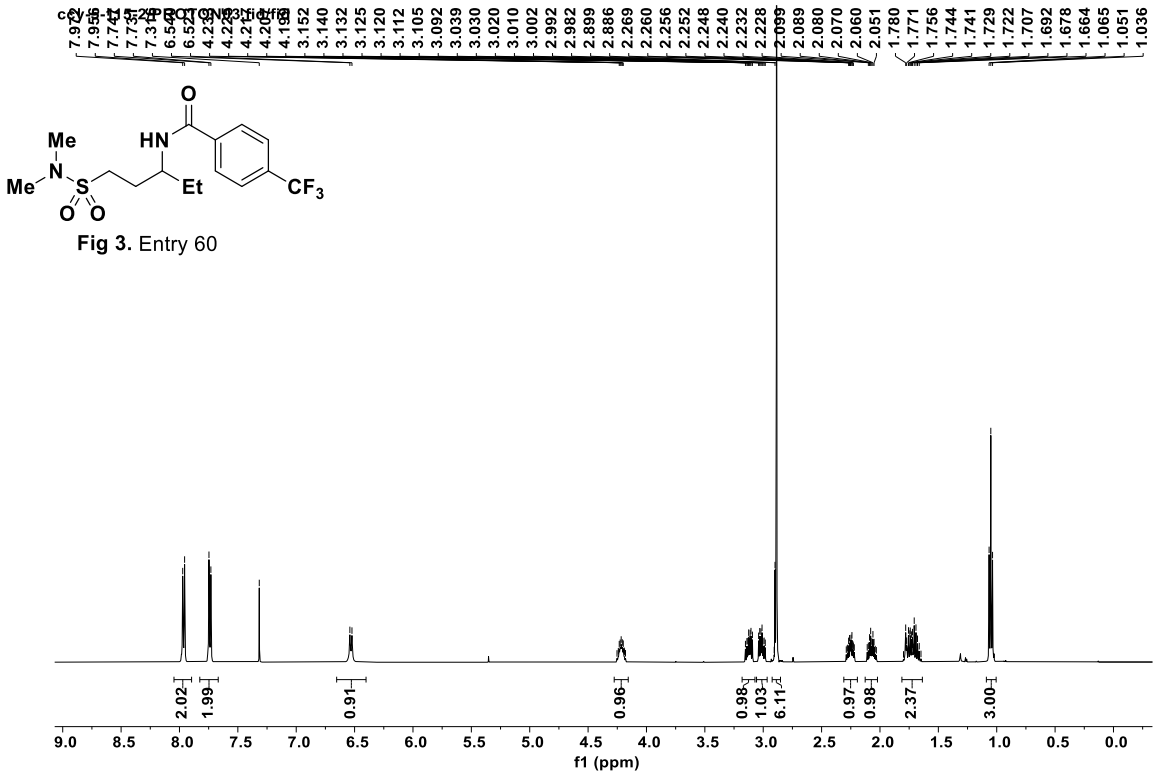

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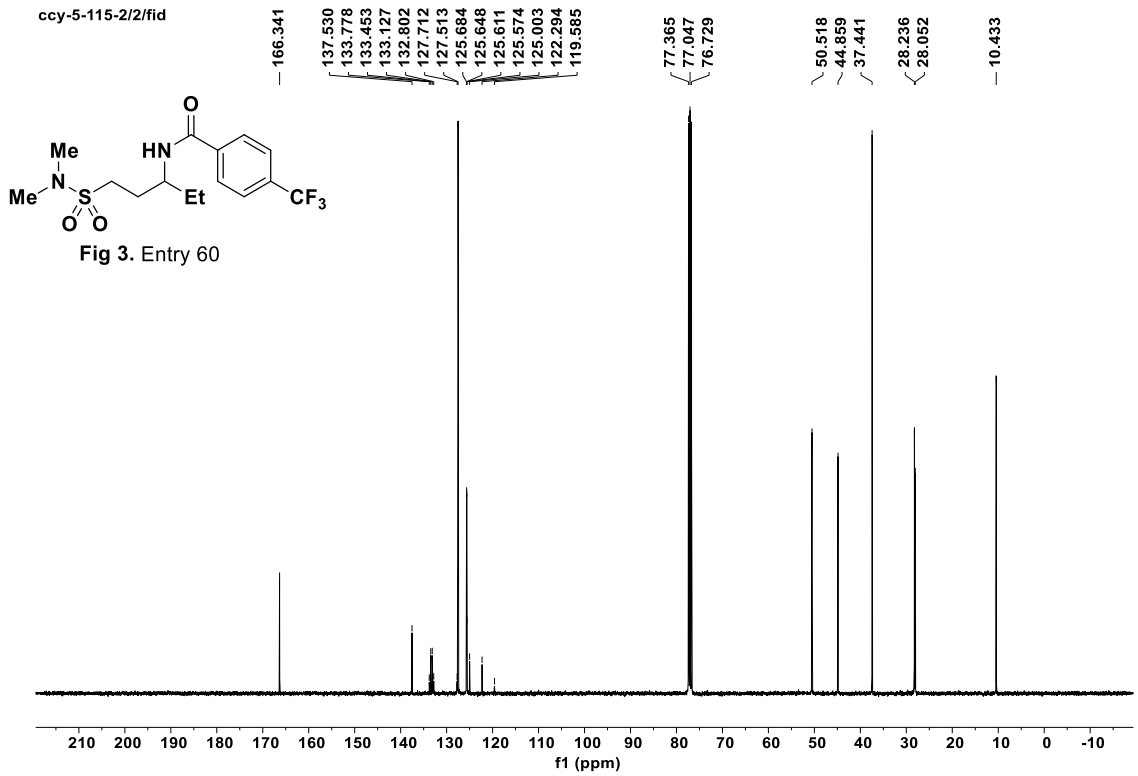

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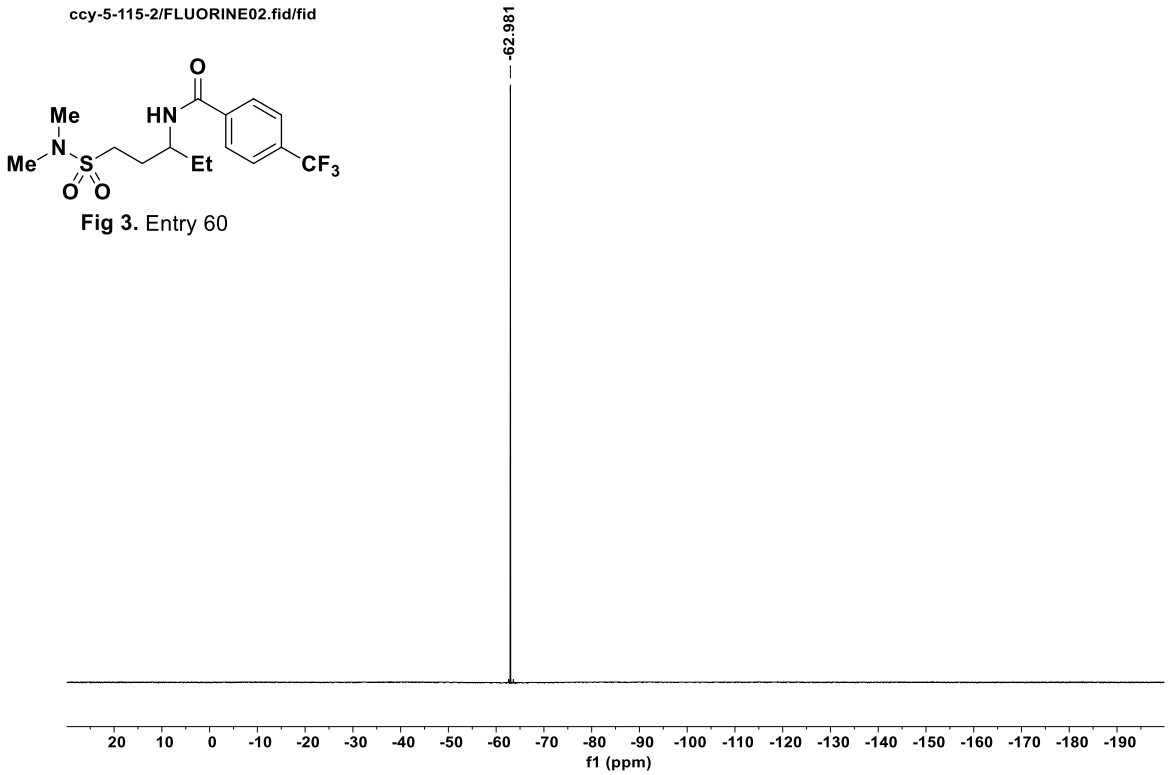

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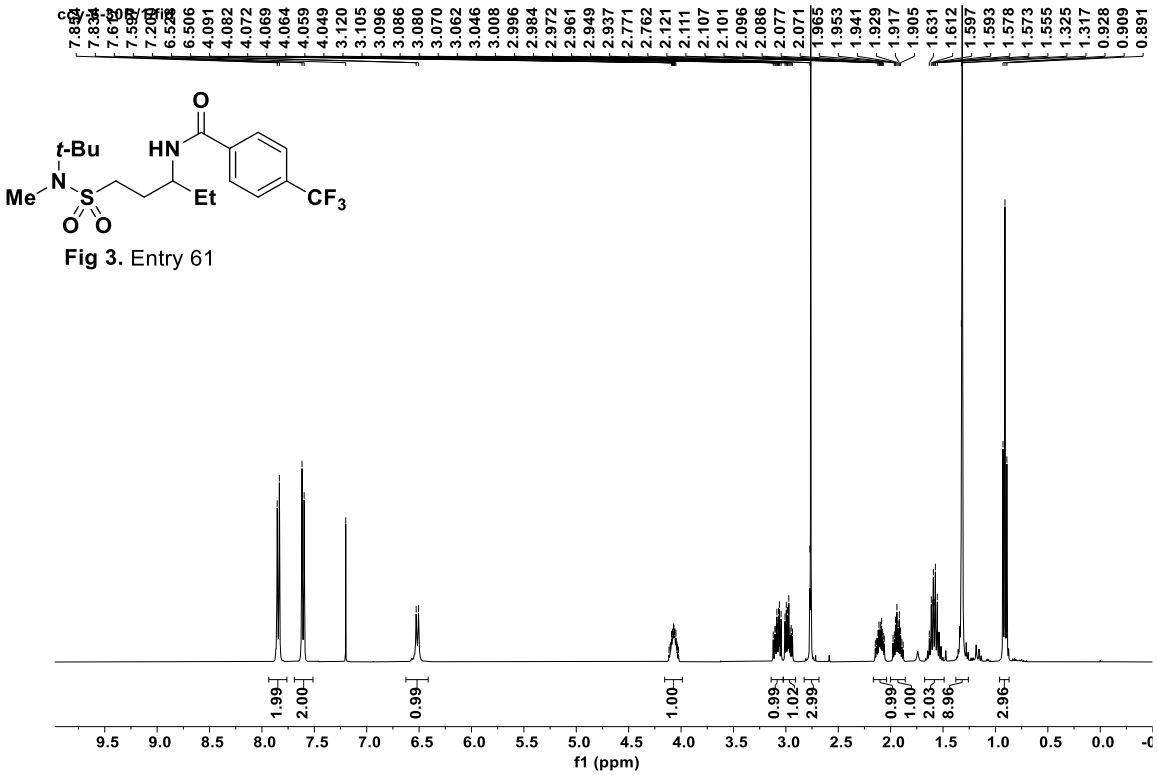

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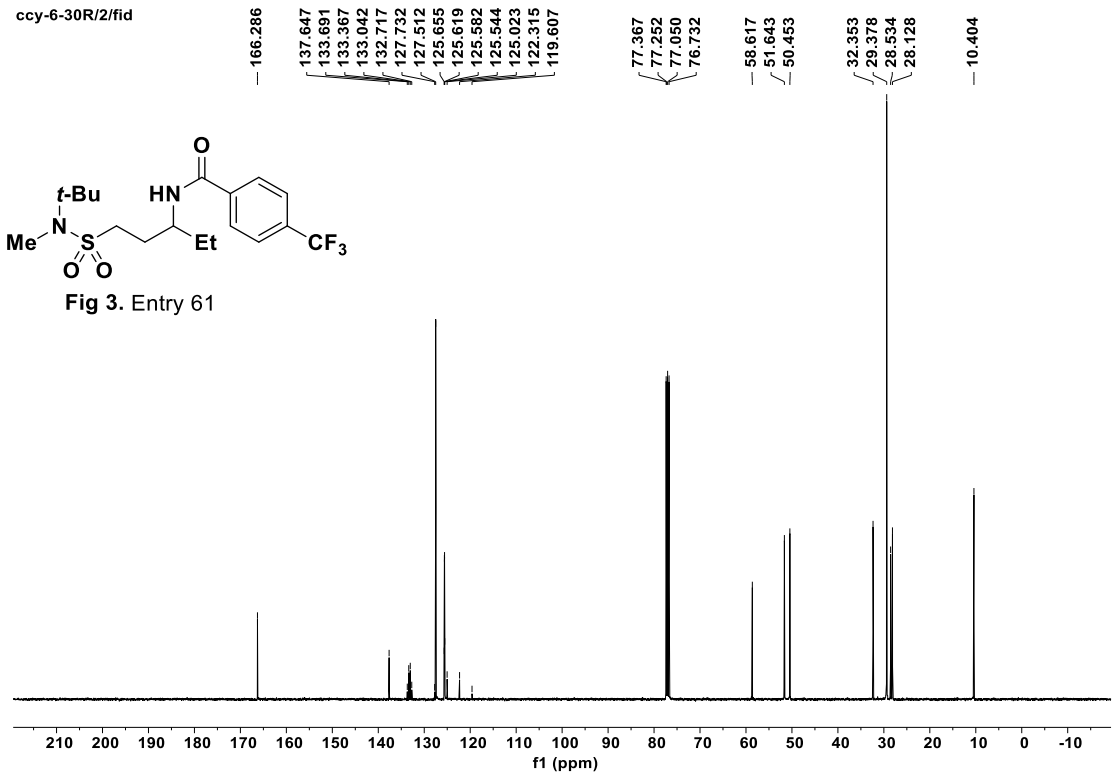

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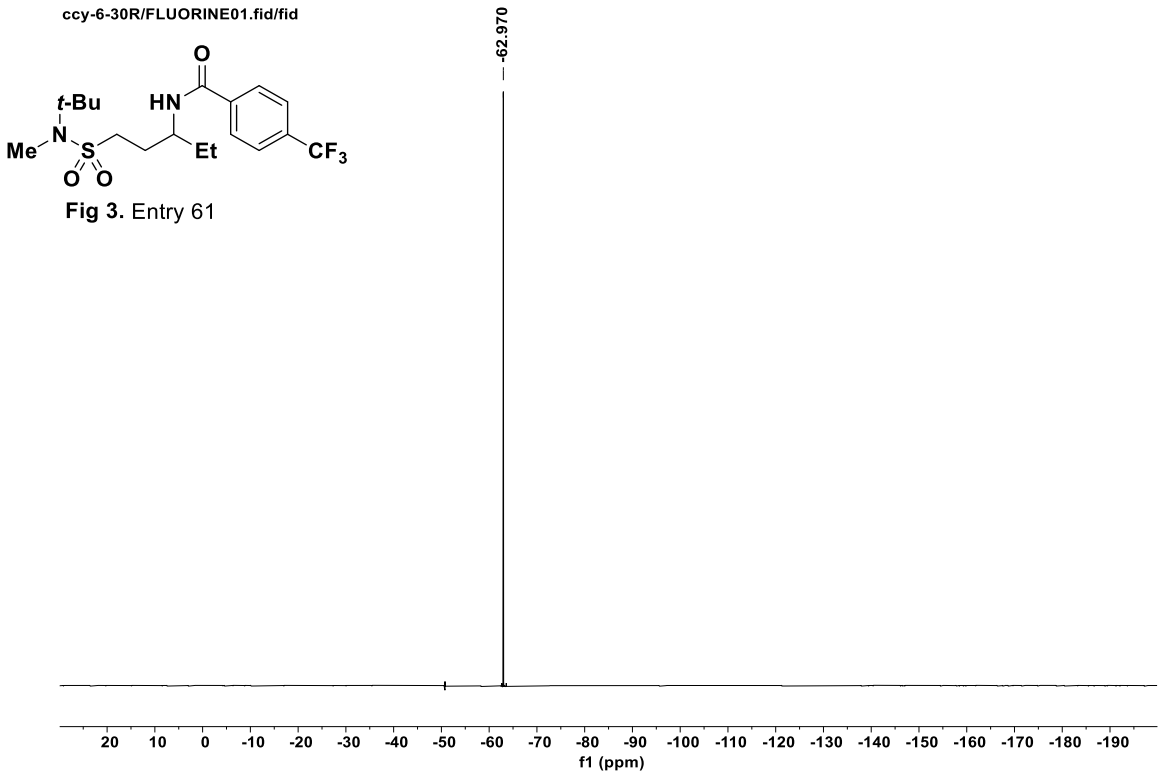

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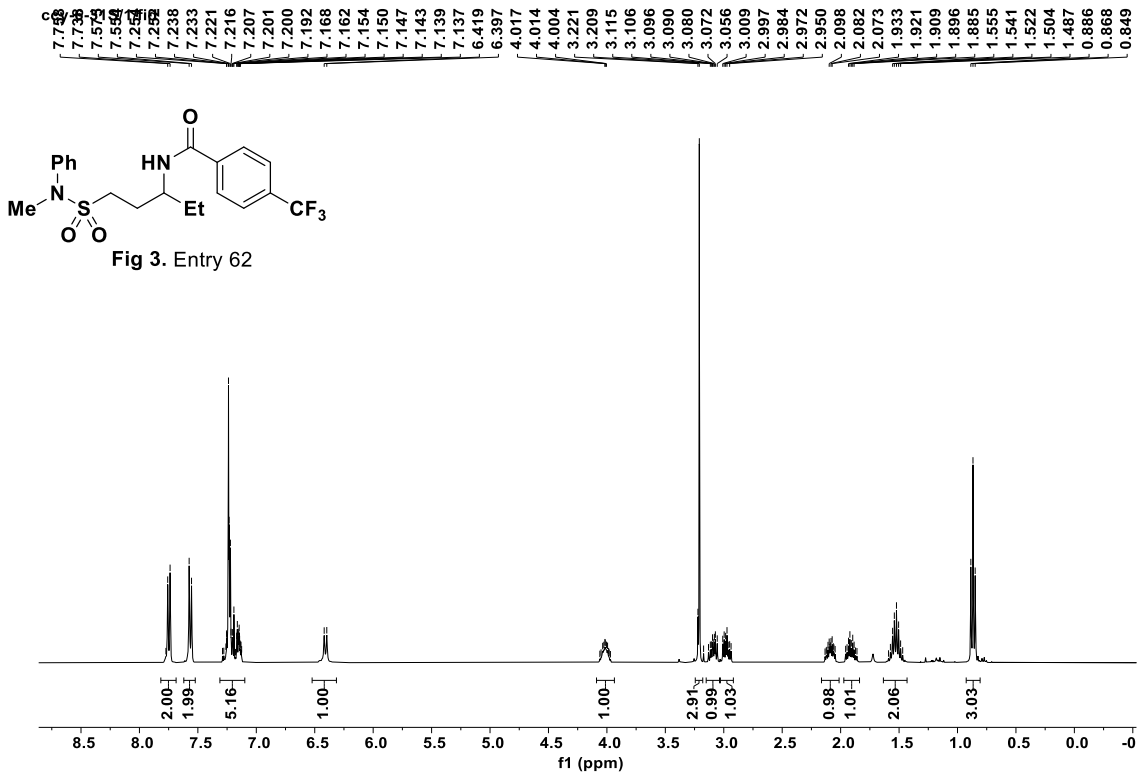

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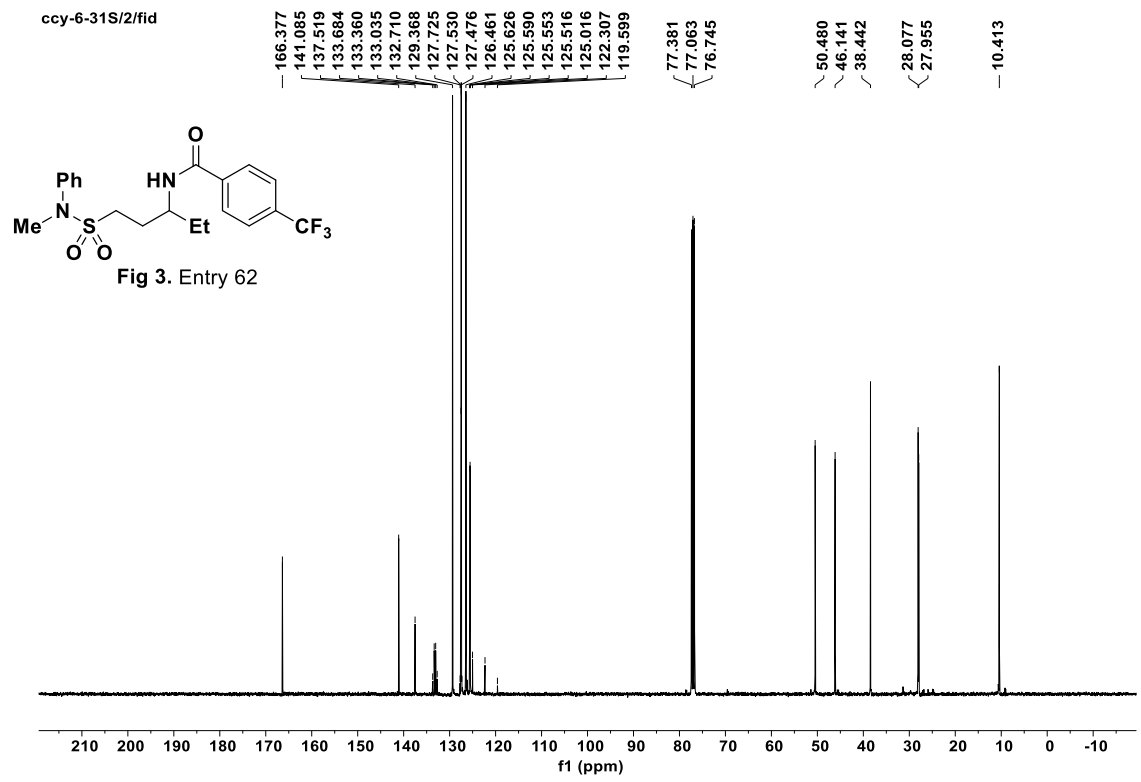


Fig 3. Entry 62

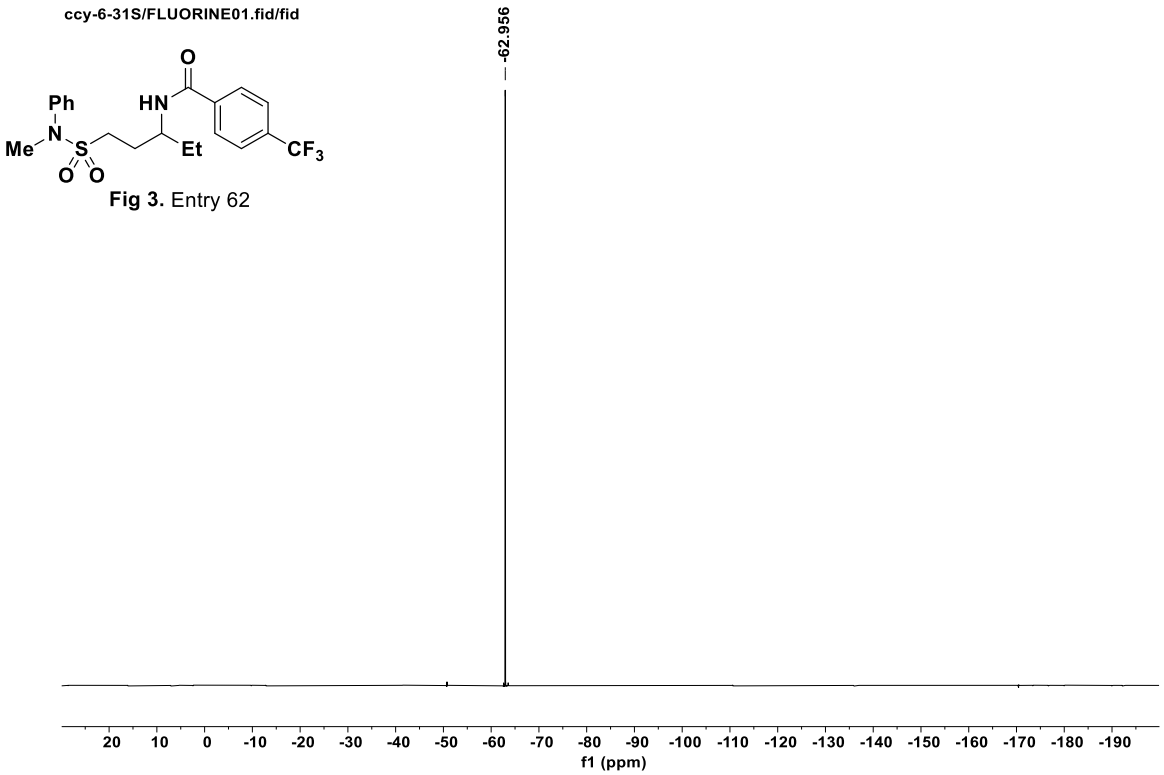


Fig 3. Entry 62

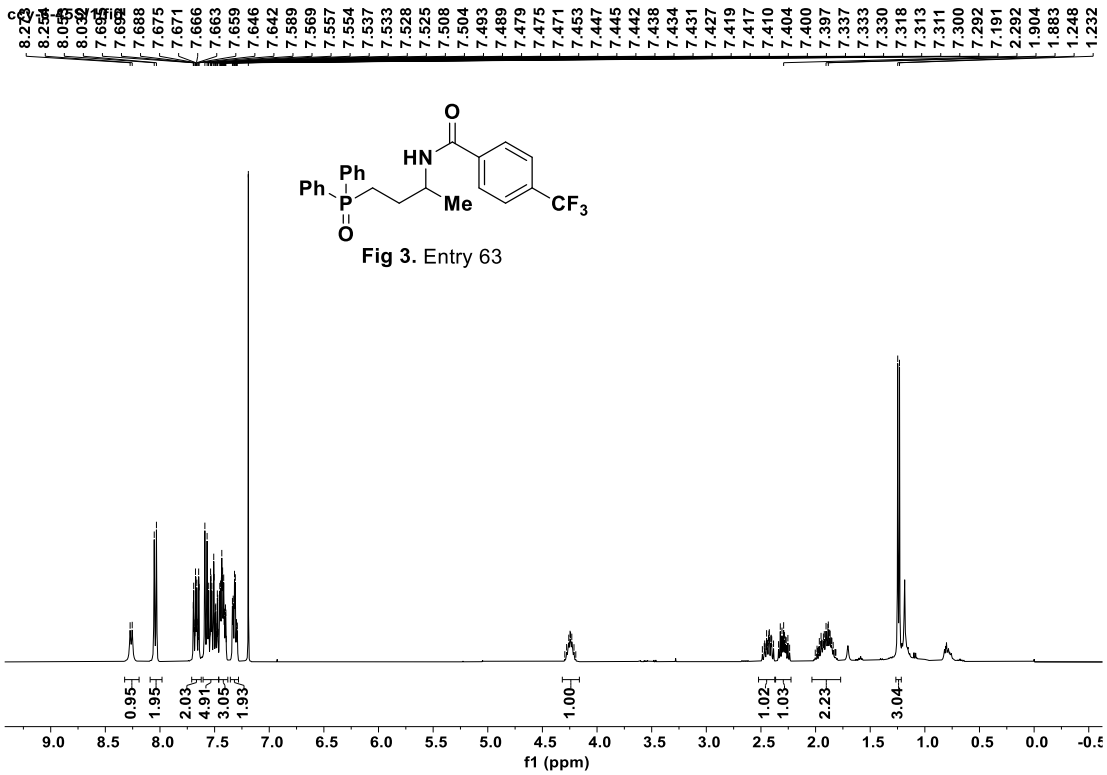


Fig 3. Entry 63

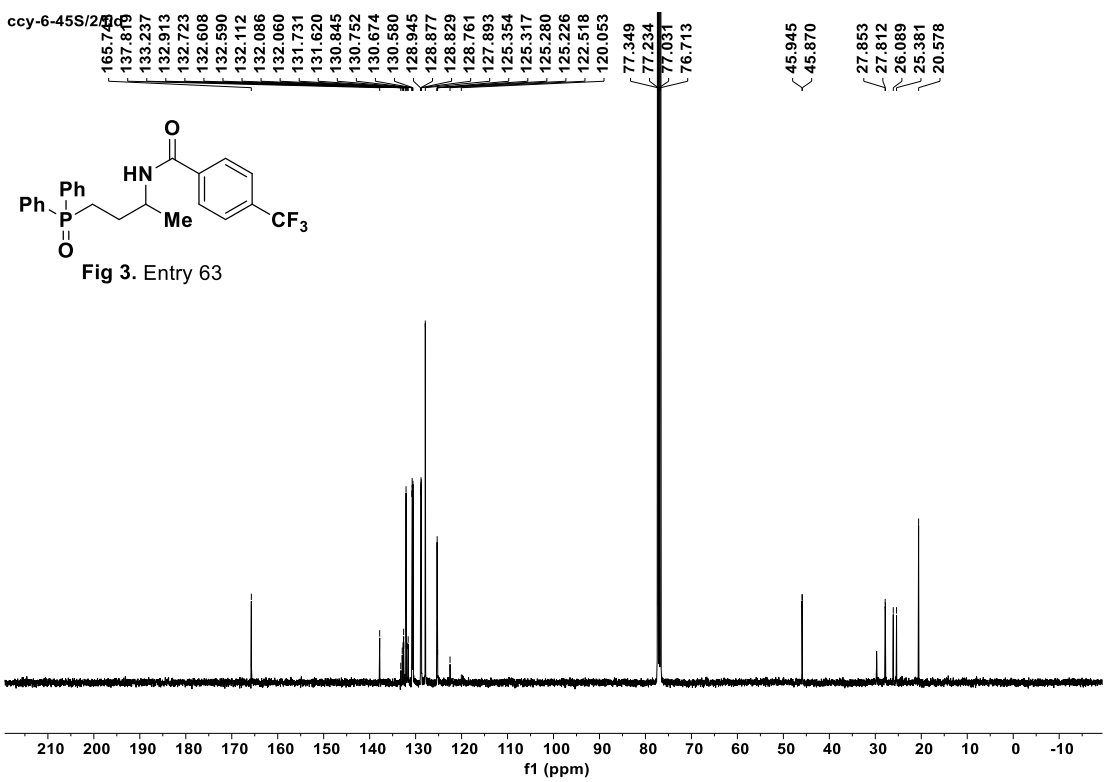


Fig 3. Entry 63

ccy-6-45S/3/fid

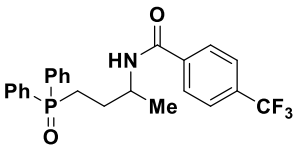


Fig 3. Entry 63

ccy-6-45S/FLUORINE01.fid/fid

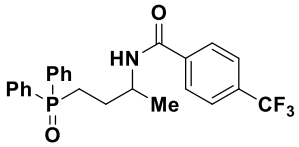
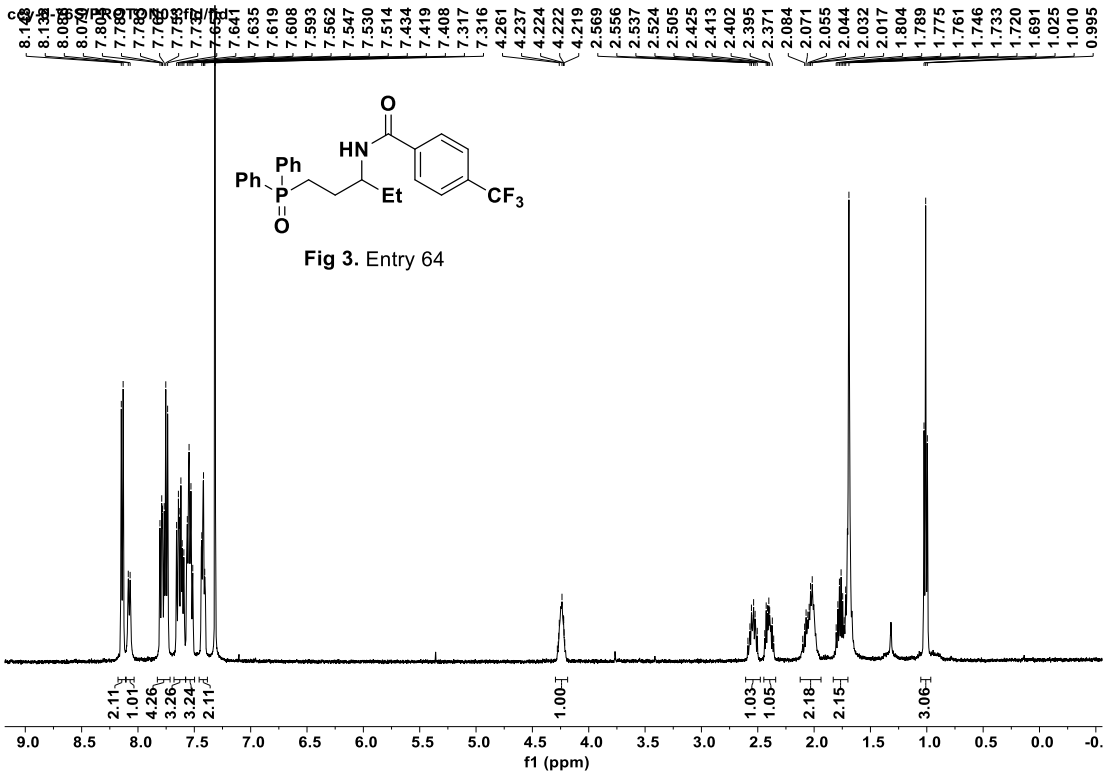


Fig 3. Entry 63



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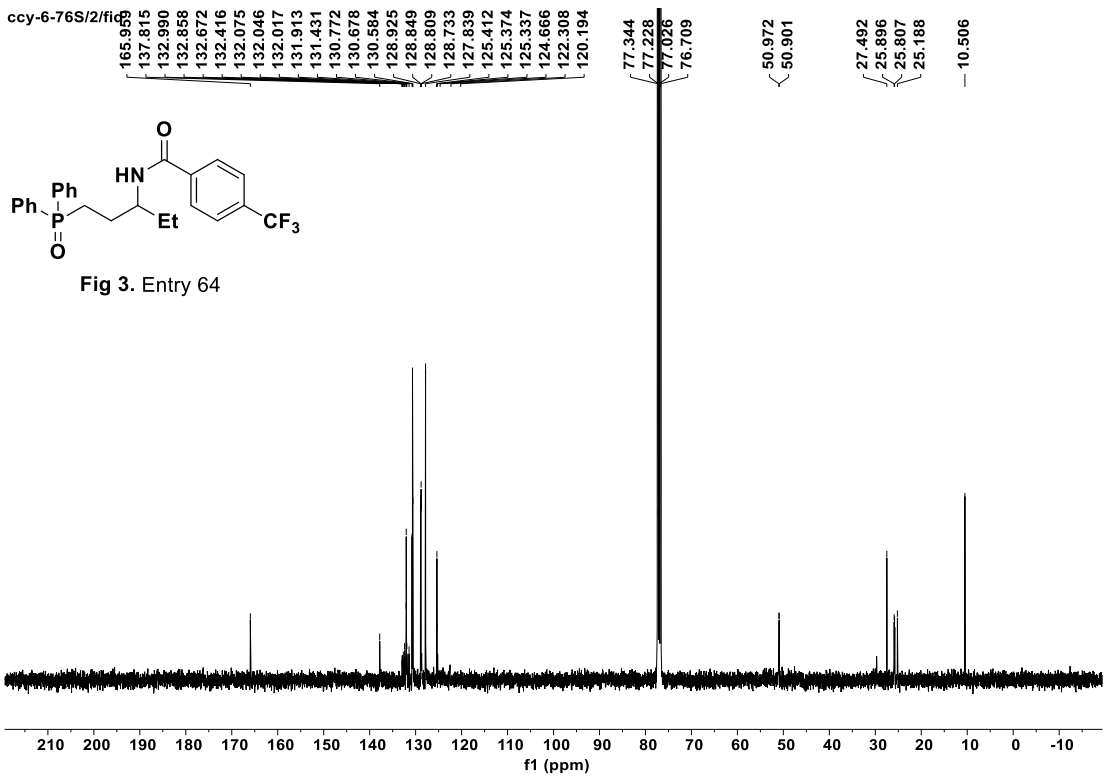

Fig 3. Entry 64

ccy-6-76S/3/fid

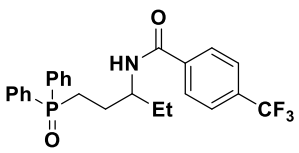

Fig 3. Entry 64

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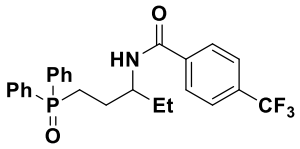
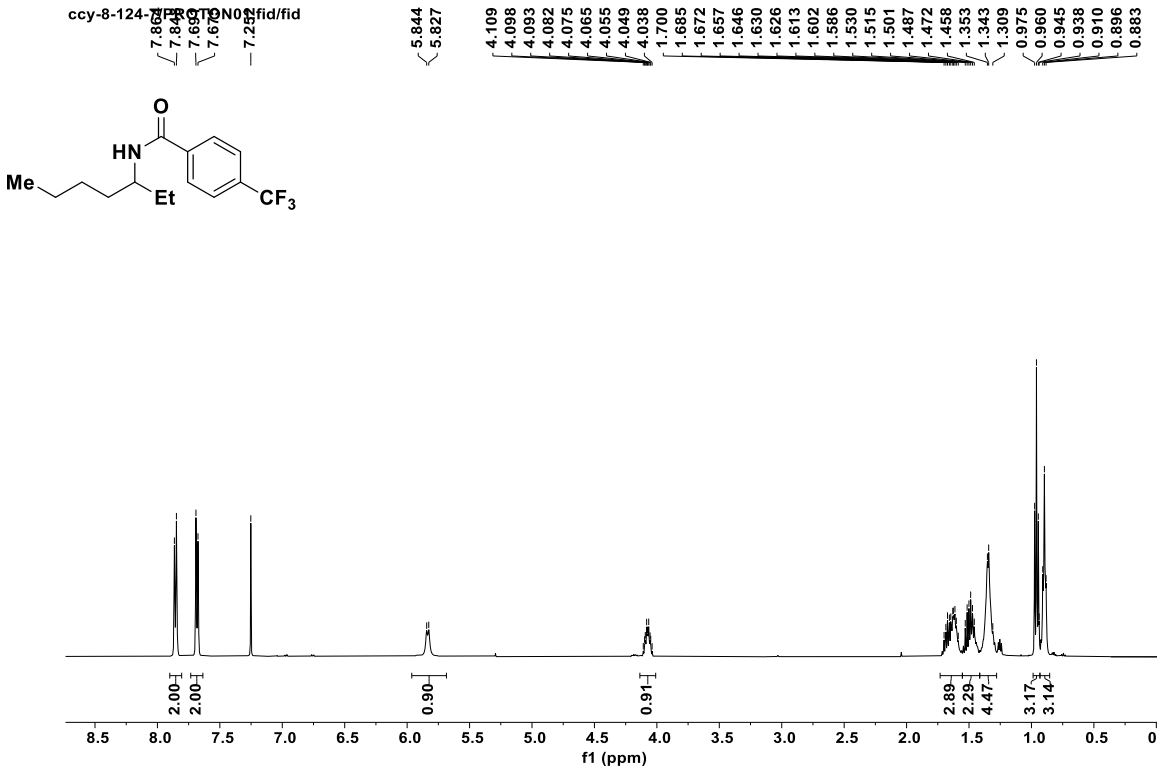


Fig 3. Entry 64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7.670
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5.827
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4.093
4.082
4.075
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4.049
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1.685
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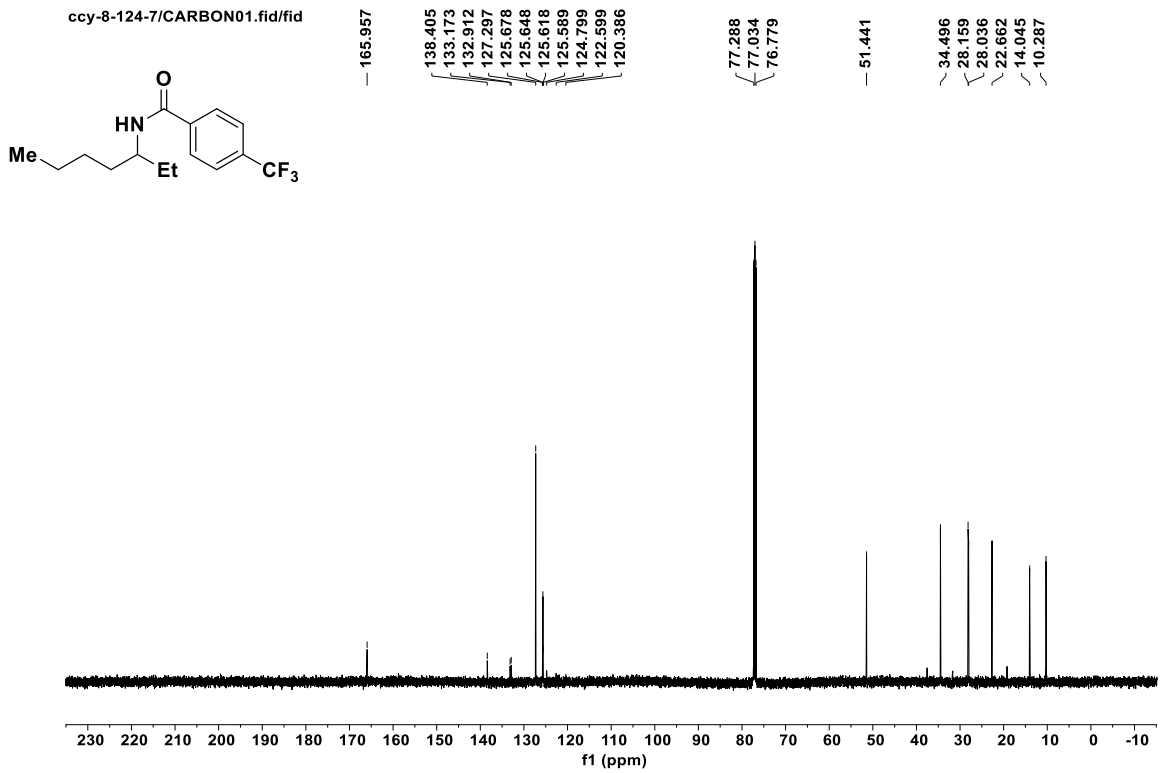
1.630
1.626
1.613
1.602
1.586
1.530
1.515
1.501
1.487
1.472
1.458
1.353
1.343
1.309
0.975
0.960
0.945
0.938
0.910
0.896
0.883
O
HN
Me
Et
CF3
2.00
2.00
0.90
0.91
2.89
2.29
4.47
3.17
3.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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120.386
77.288
77.034
76.779
51.441
34.496
28.159
28.036
22.662
14.045
10.287
O
HN
Me
Et
CF3
230
220
210
200
190
180
170
160
150
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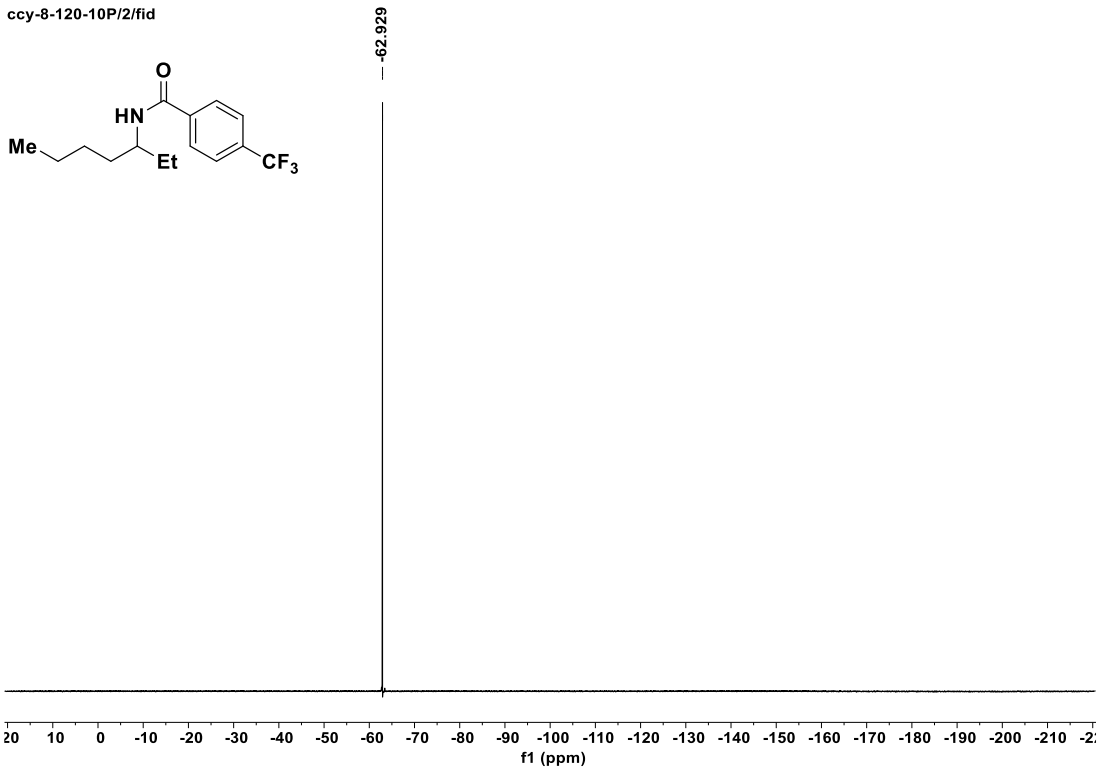
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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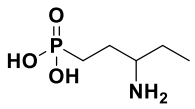
-62.929
O
HN
Me
Et
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

ccy-6-139/PROTON02.fid/fid



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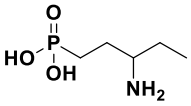

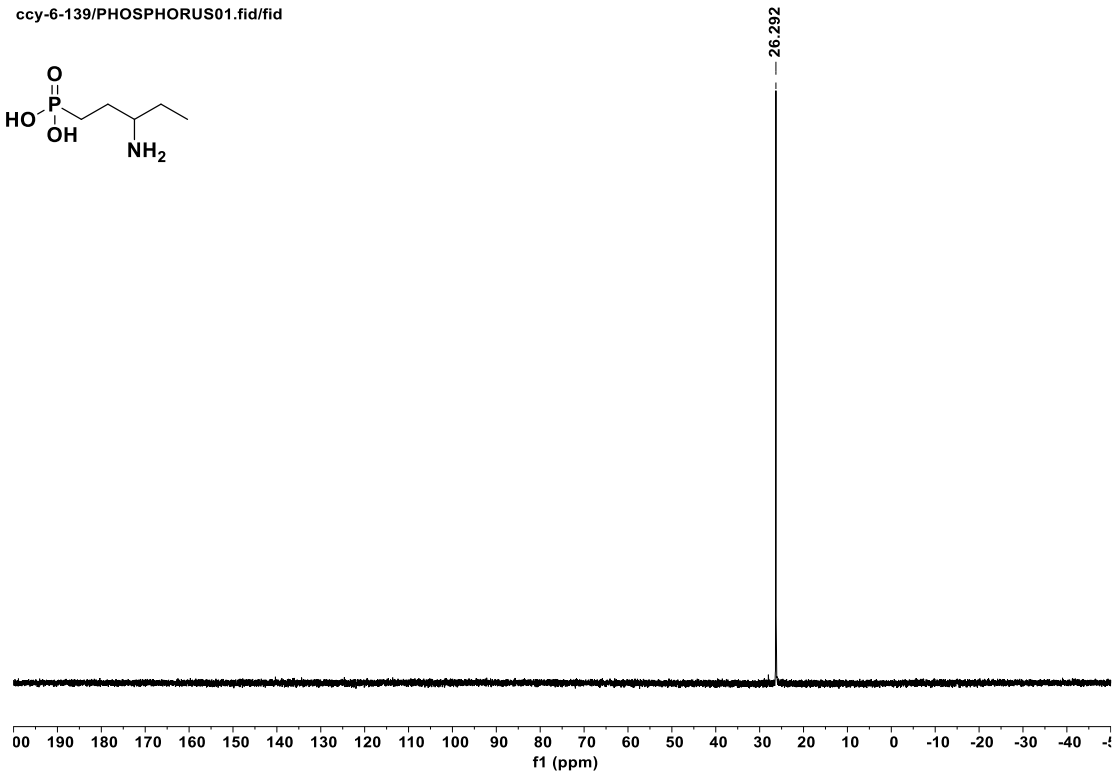
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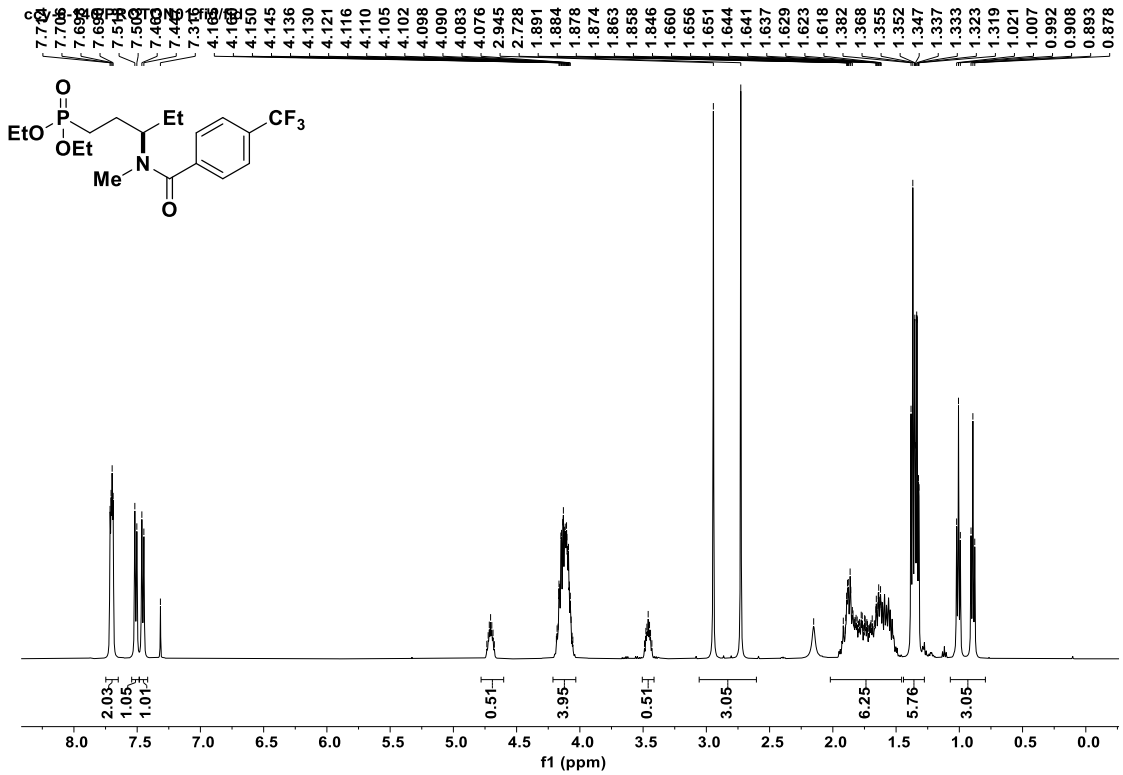
f1 (ppm)


O
EtO
P
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Et
CF3
N
Me
O
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3.05
6.25
5.76
3.05
8.0
7.5
7.0
6.5
6.0
5.5
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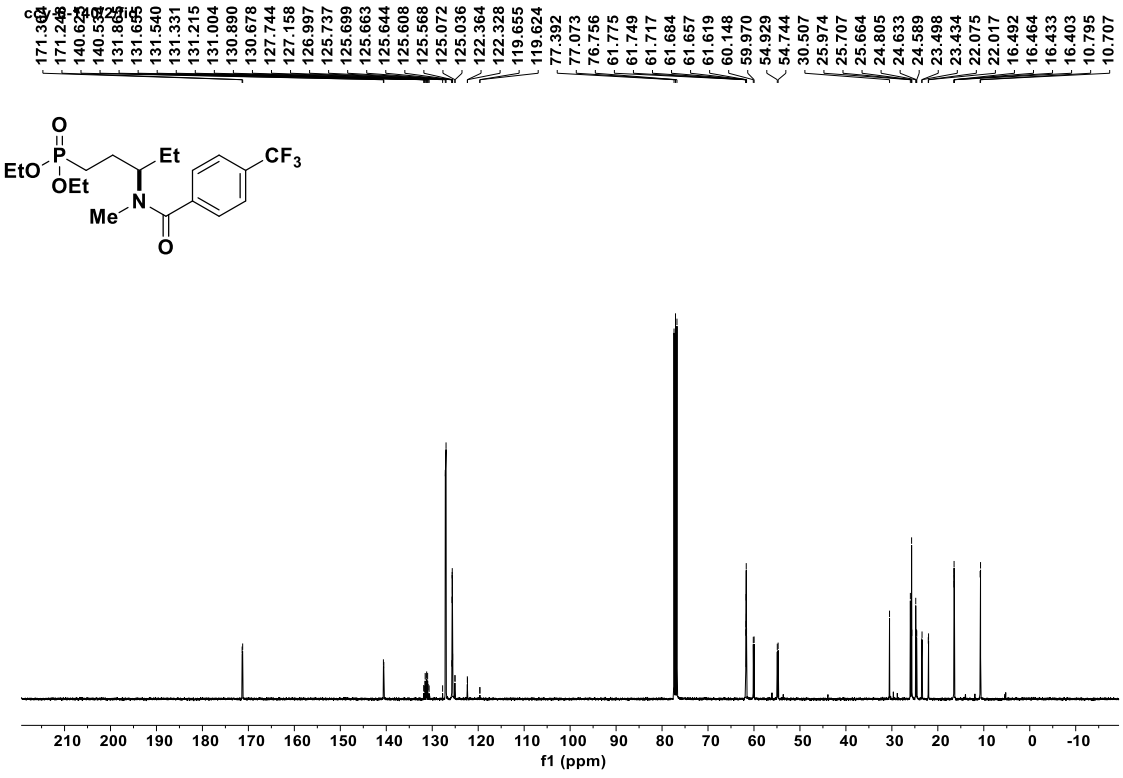
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
EtO
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Et
CF3
N
Me
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200
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180
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160
150
140
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100
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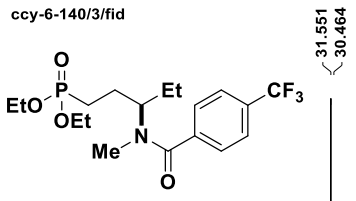
70
60
50
40
30
20
10
0
-10
f1 (ppm)

ccy-6-140/3/fid



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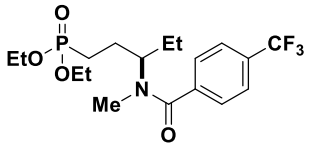
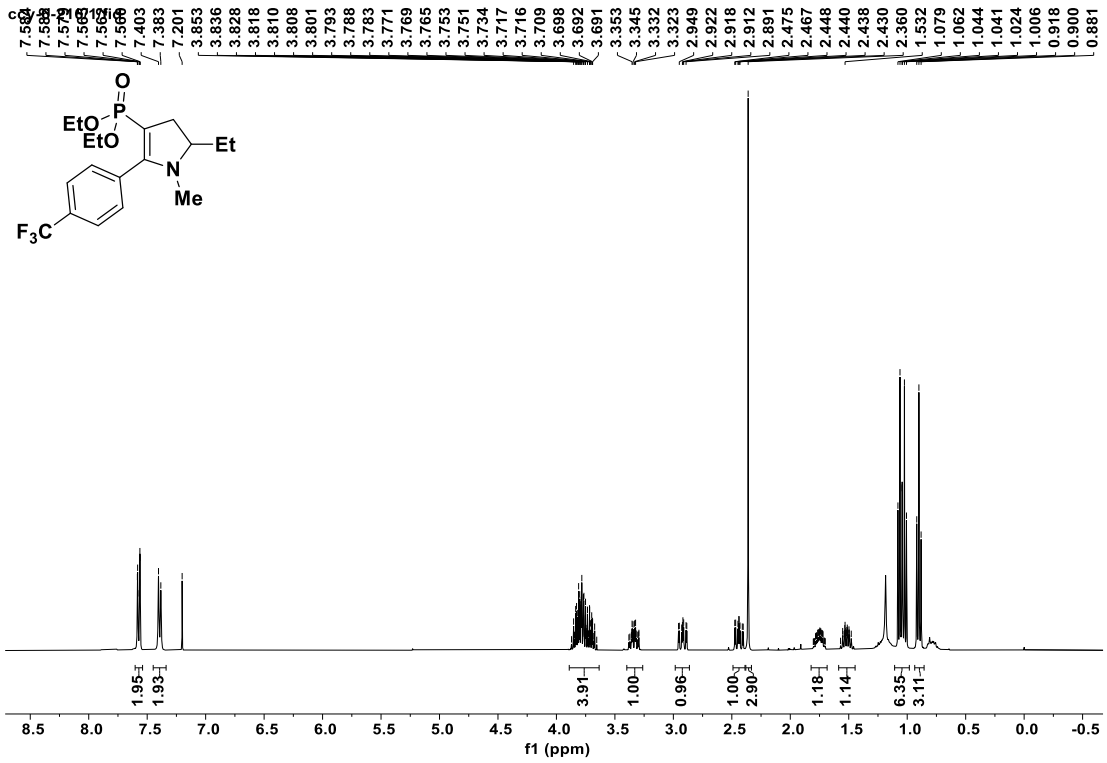
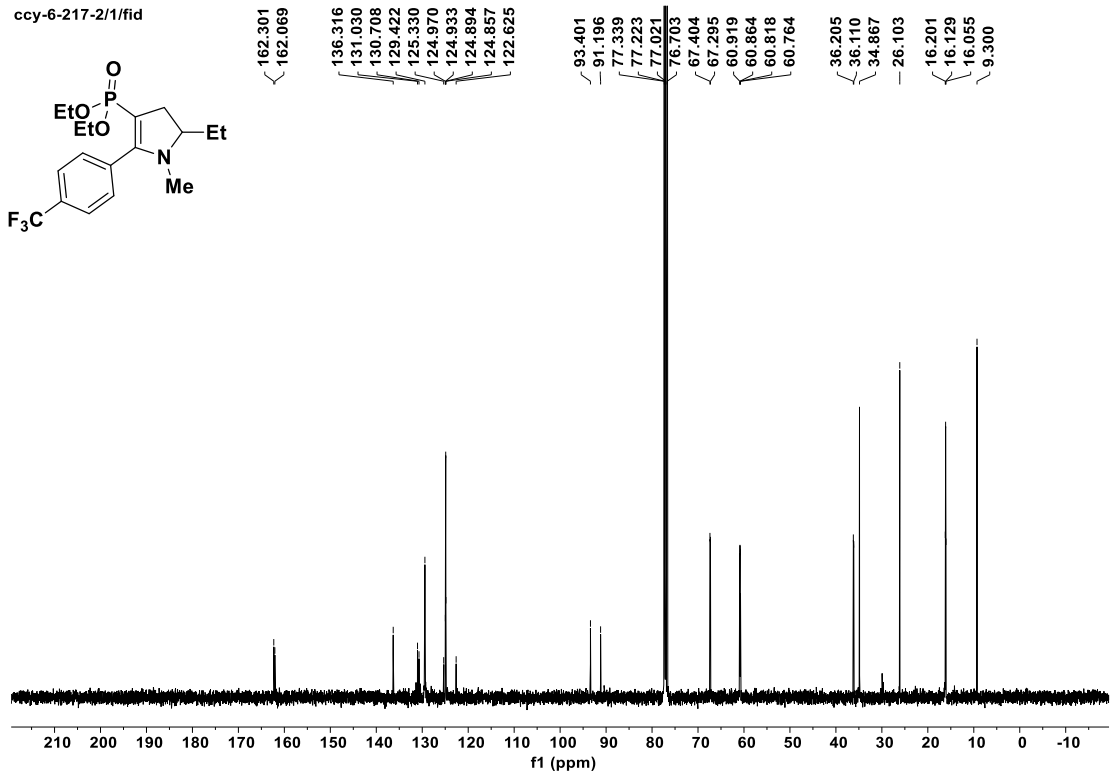
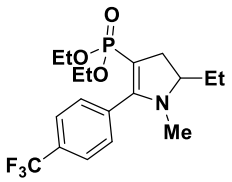


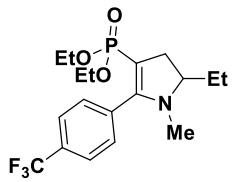

ccy-6-217-2/1/fid
7.582
7.580
7.579
7.566
7.565
7.403
7.383
7.201
3.853
3.836
3.828
3.818
3.810
3.808
3.801
3.793
3.788
3.783
3.771
3.769
3.765
3.753
3.751
3.734
3.717
3.716
3.709
3.698
3.692
3.691
3.353
3.345
3.332
3.323
2.949
2.922
2.918
2.912
2.891
2.475
2.467
2.448
2.440
2.438
2.430
2.360
1.532
1.079
1.062
1.044
1.041
1.024
1.006
0.918
0.900
0.881
O
P
EtO
EtO
Et
N
Me
F3C
1.95
1.93
3.91
1.00
0.96
1.00
2.90
1.18
1.14
6.35
3.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

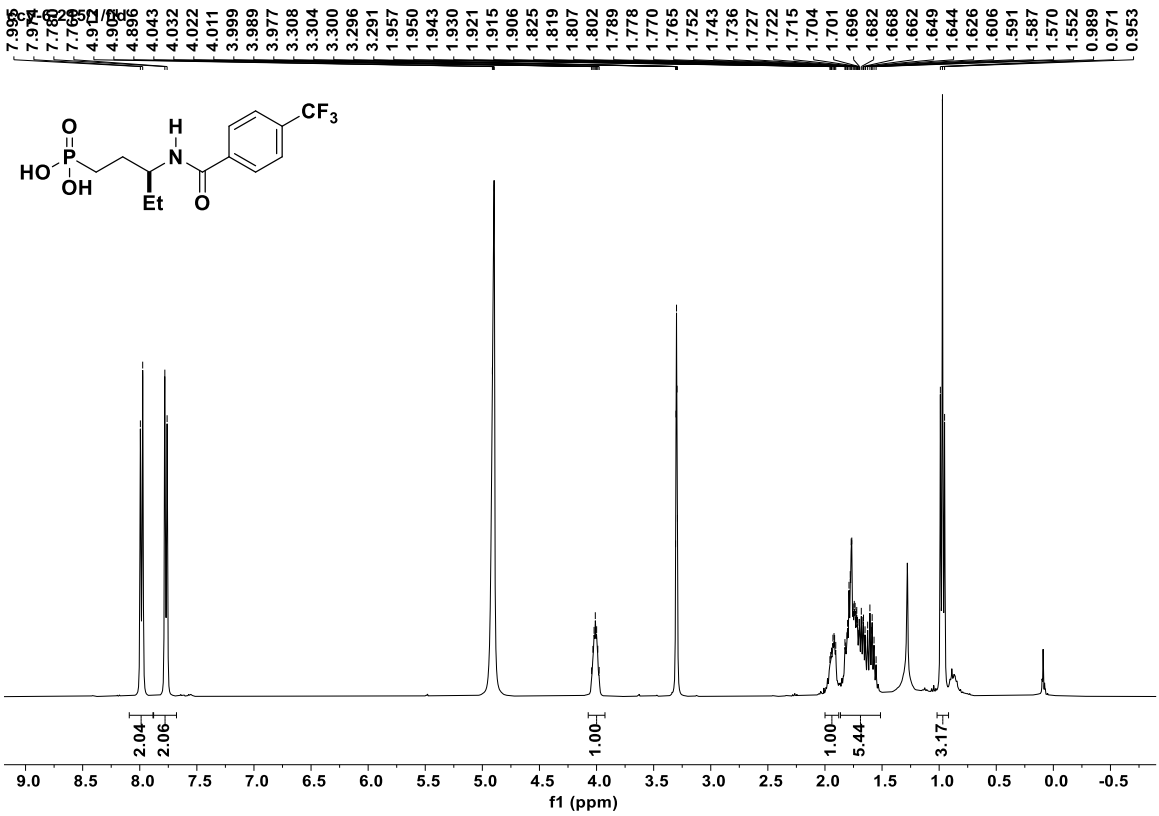

ccy-6-217-2/1/fid
162.301
162.069
136.316
131.030
130.708
129.422
125.330
124.970
124.933
124.894
124.857
122.625
93.401
91.196
77.339
77.223
77.021
76.703
67.404
67.295
60.919
60.864
60.818
60.764
36.205
36.110
34.867
26.103
16.201
16.129
16.055
9.300
O
P
EtO
EtO
Et
N
Me
F3C
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

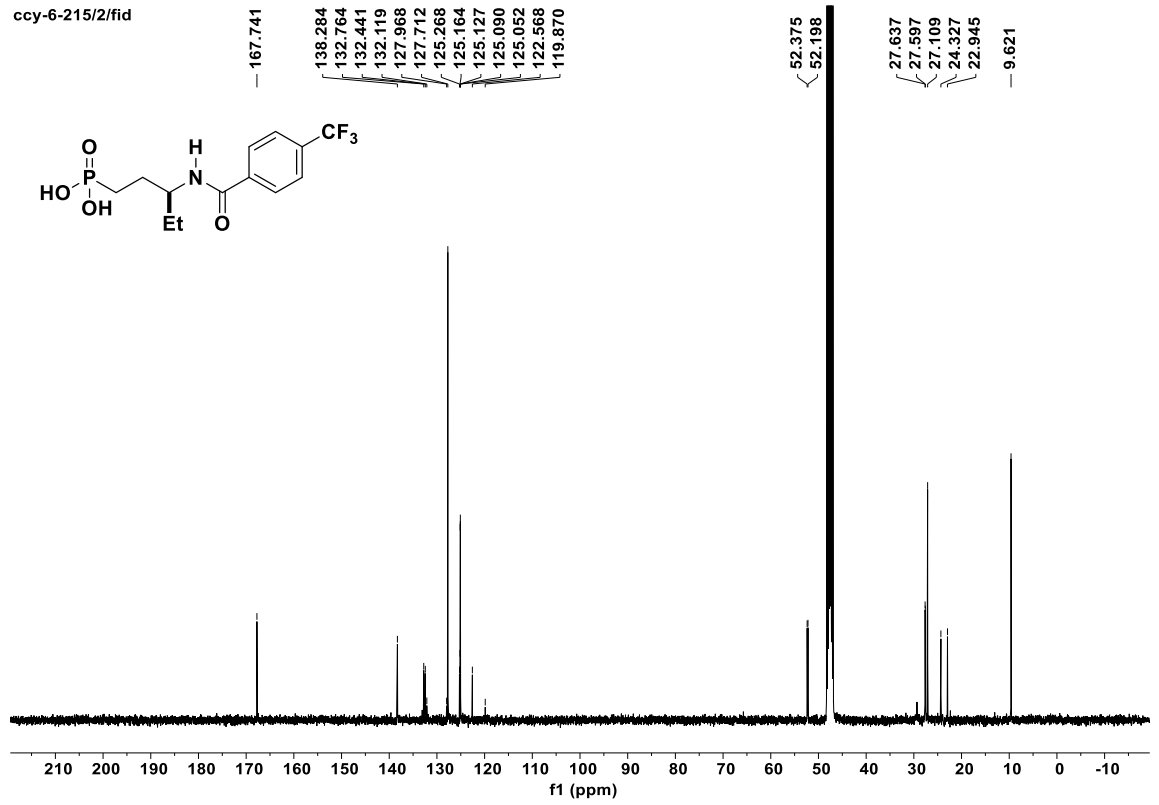
ccy-6-216/3/fid

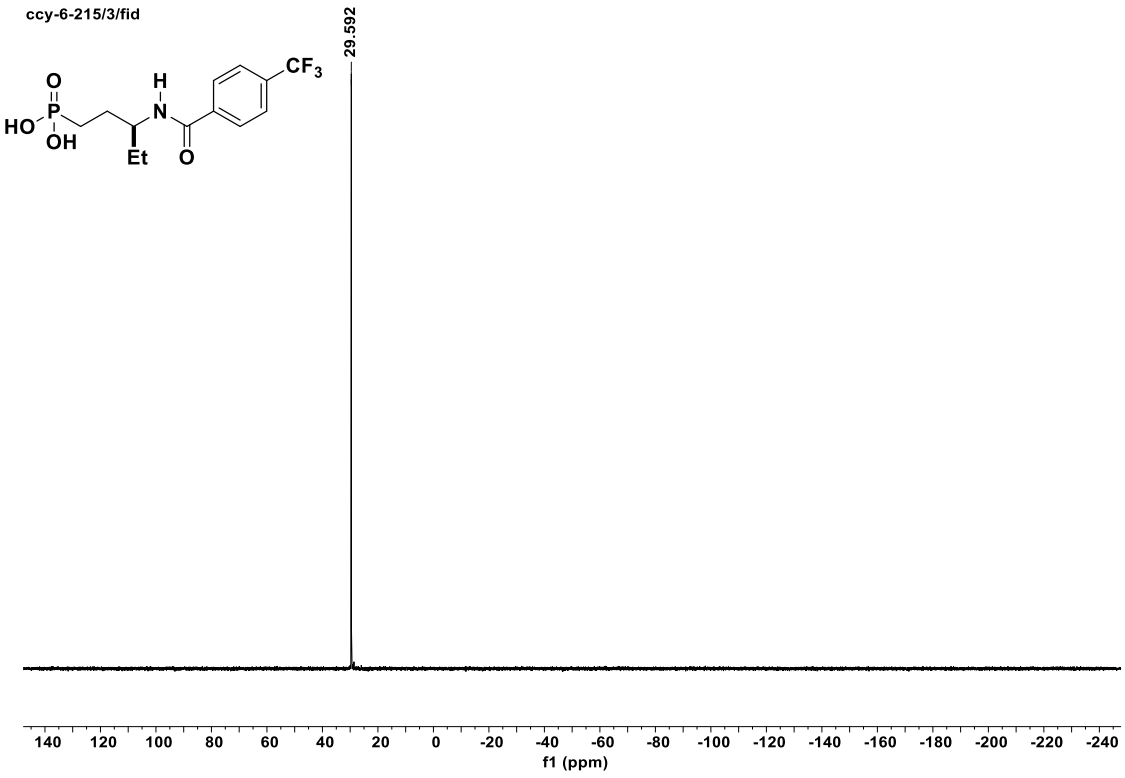


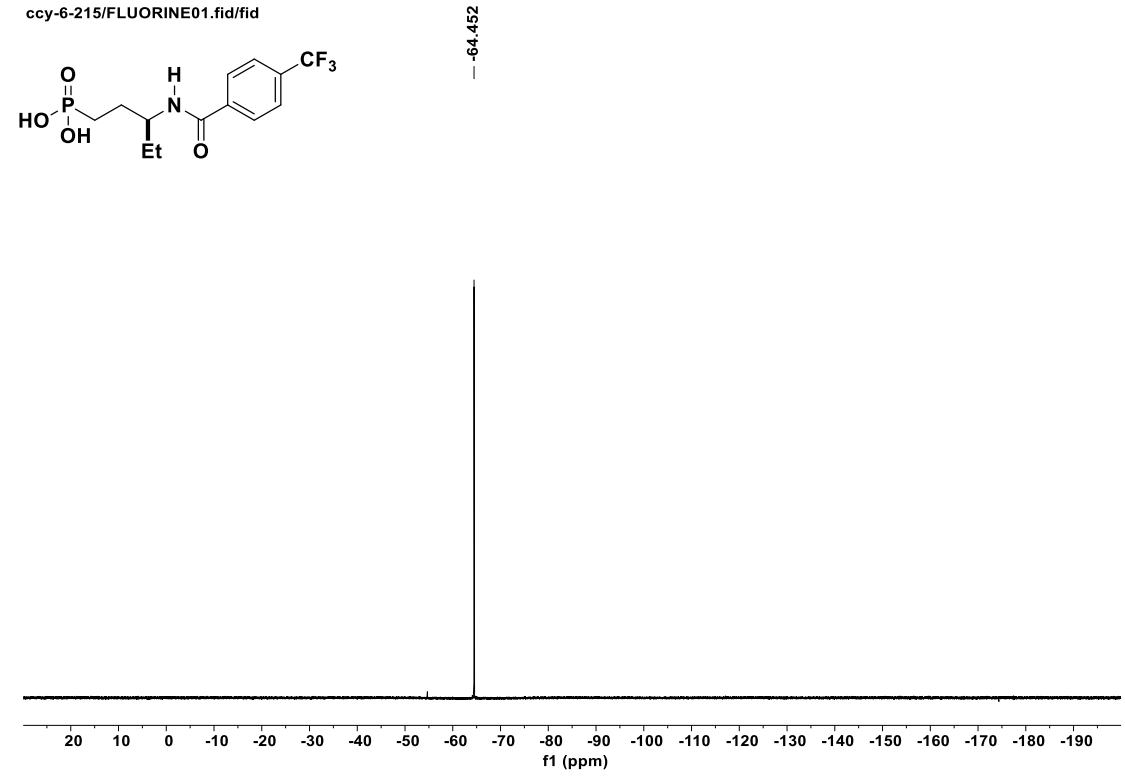
ccy-6-216/FLUORINE01.fid/fid

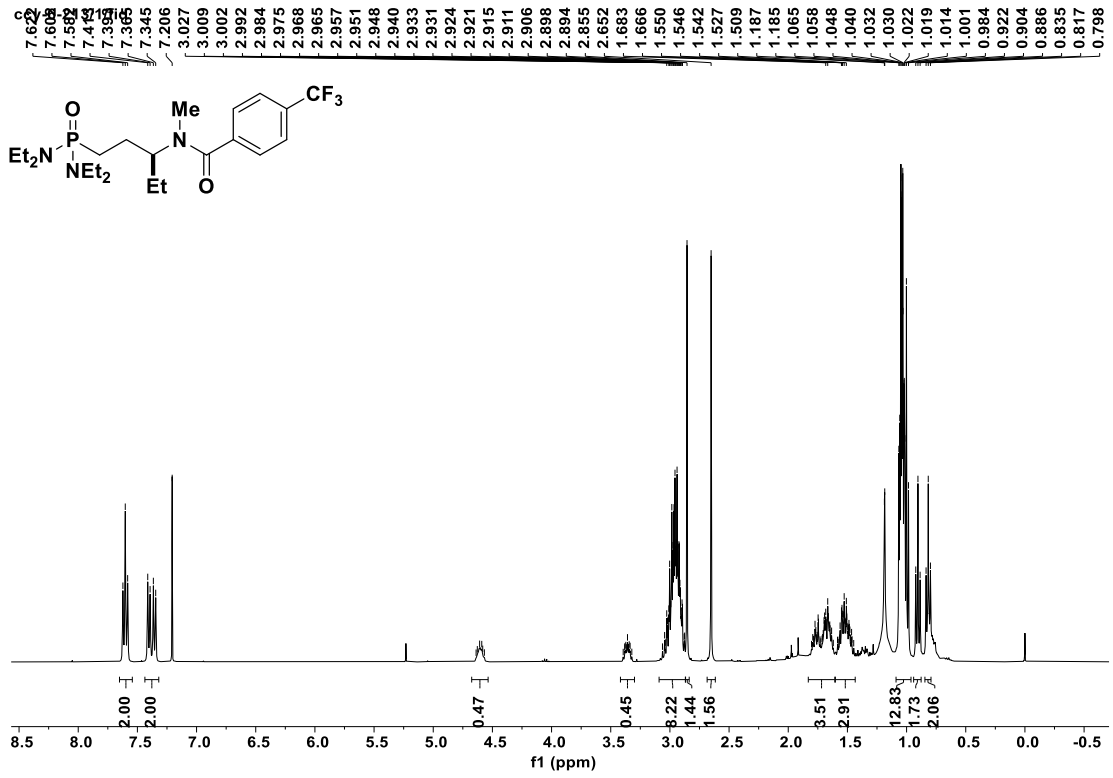


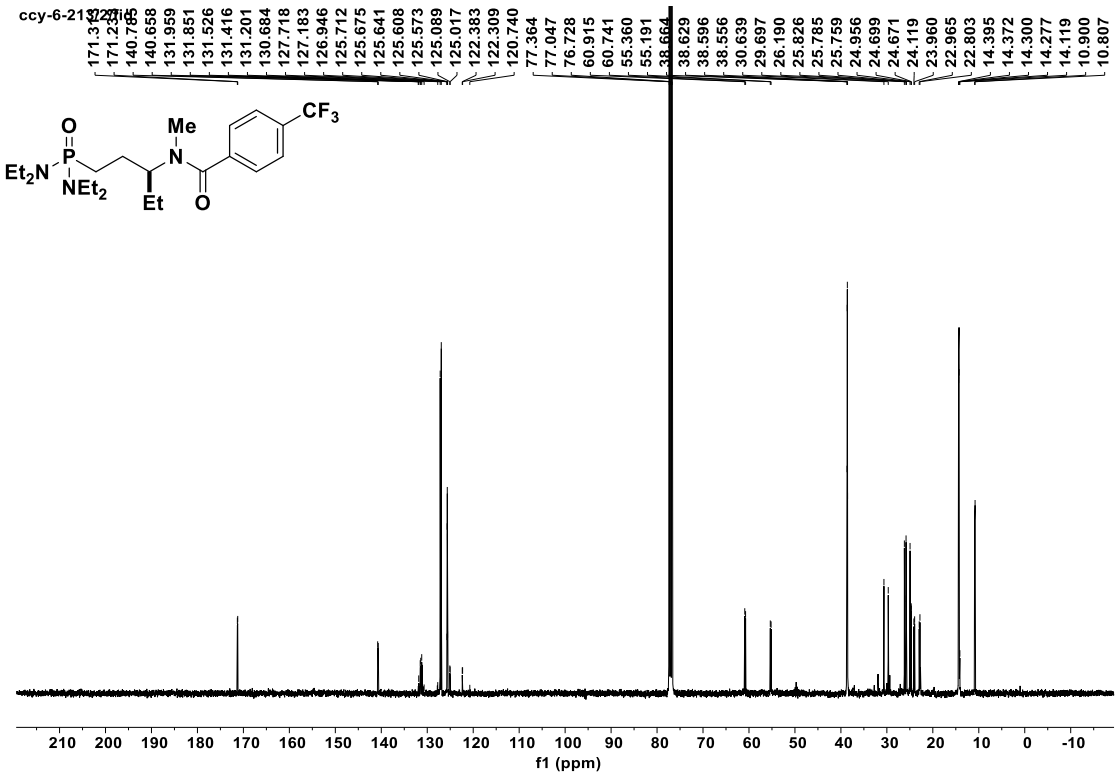

ccy-6-225/1/fid
7.995 7.978 7.776 7.760 4.911 4.896 4.043 4.032 4.022 4.011 3.999 3.989 3.977 3.308 3.304 3.300 3.296 3.291 1.957 1.950 1.943 1.930 1.921 1.915 1.906 1.825 1.819 1.807 1.802 1.789 1.778 1.770 1.765 1.752 1.743 1.736 1.727 1.722 1.715 1.704 1.701 1.696 1.682 1.668 1.662 1.649 1.644 1.626 1.606 1.591 1.587 1.570 1.552 0.989 0.971 0.953
HO
P
O
OH
H
N
Et
O
CF3
2.04
2.06
1.00
1.00
5.44
3.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

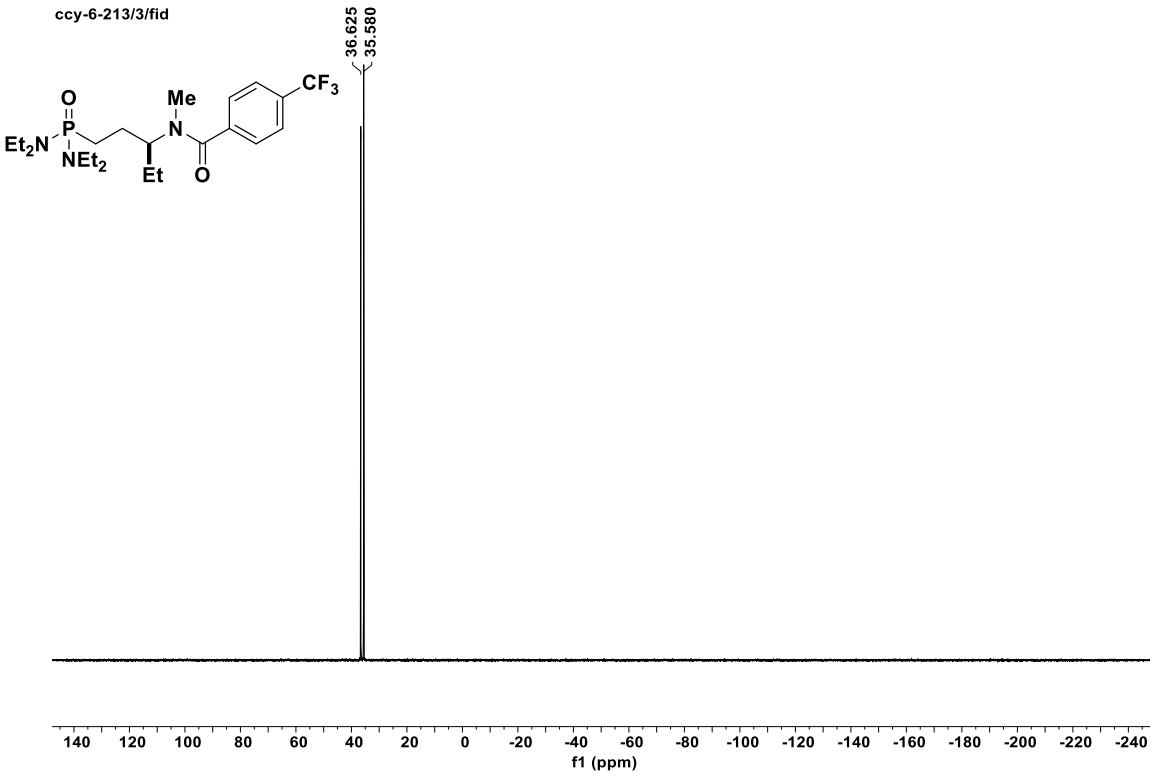

ccy-6-215/2/fid
167.741
138.284 132.764 132.441 132.119 127.968 127.712 125.268 125.164 125.127 125.090 125.052 122.568 119.870
52.375 52.198
27.637 27.597 27.109 24.327 22.945
9.621
HO
P
O
OH
H
N
Et
O
CF3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

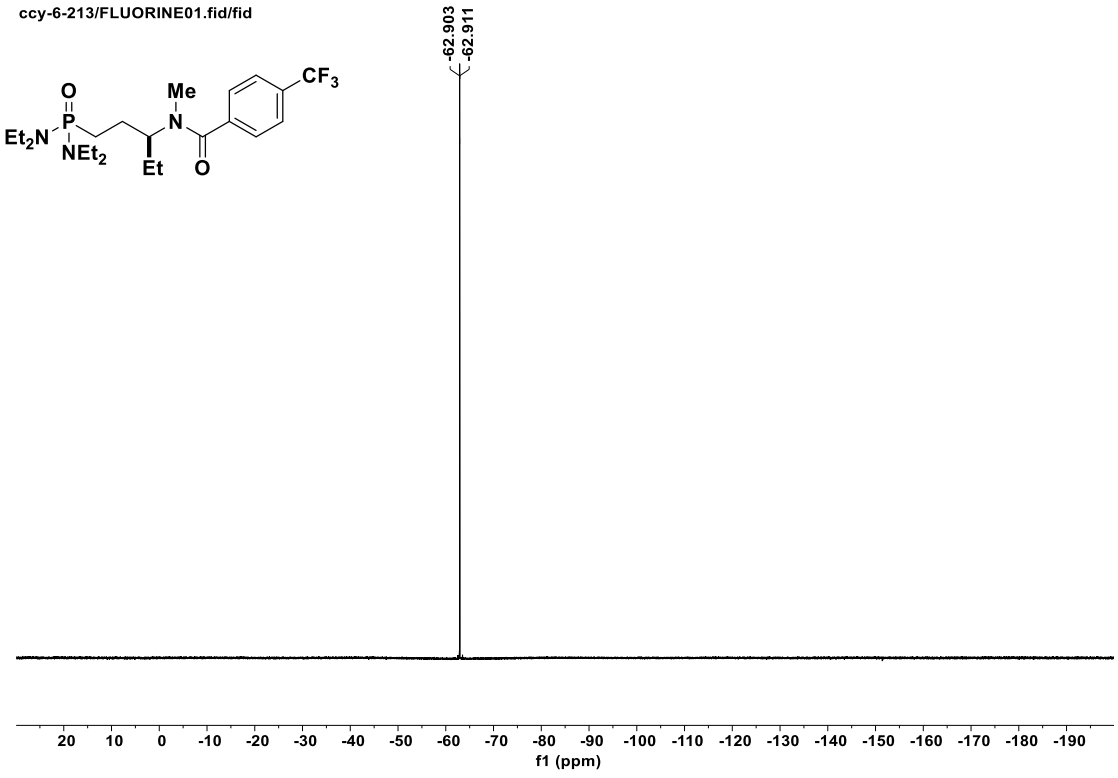

ccy-6-215/3/fid
29.592
HO
O
P
OH
H
N
Et
O
CF3
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

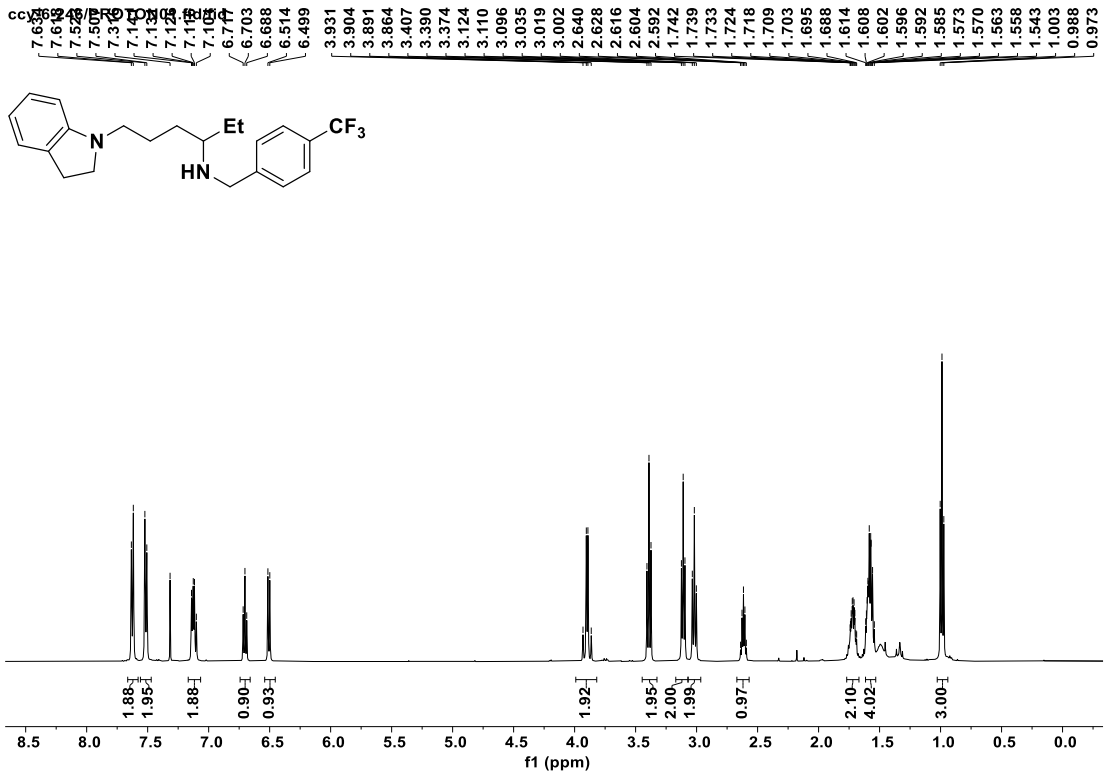

ccy-6-215/FLUORINE01.fid/fid
-64.452
HO
O
P
OH
H
N
Et
O
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

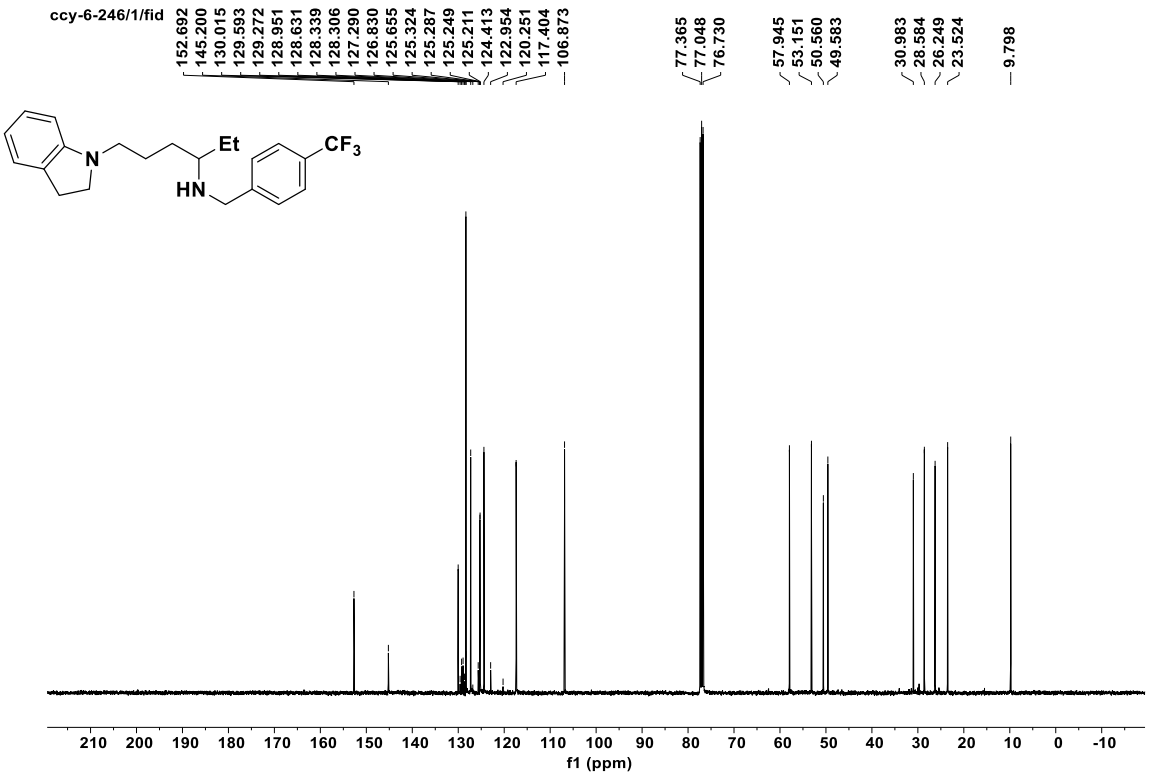

Et2N
NEt2
O
P
Me
N
Et
O
CF3
2.00
2.00
0.47
0.45
8.22
1.44
1.56
3.51
2.91
12.83
1.73
2.06
f1 (ppm)

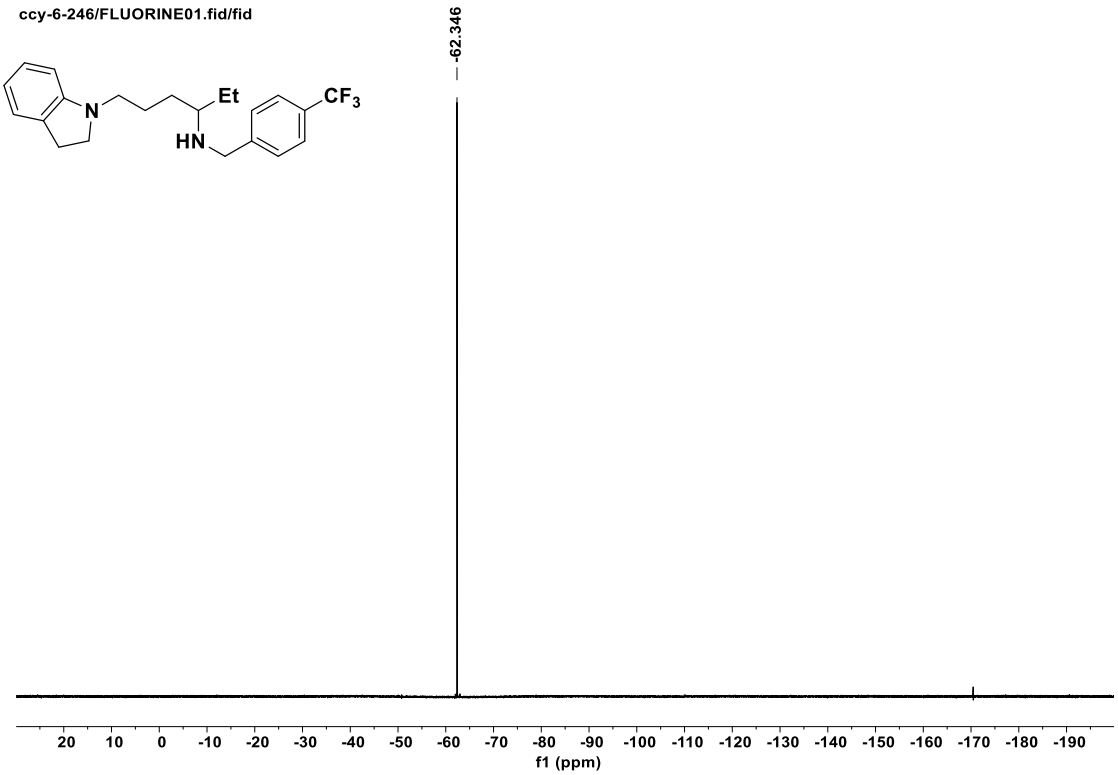

Et2N
NEt2
O
P
Me
N
Et
O
CF3
f1 (ppm)

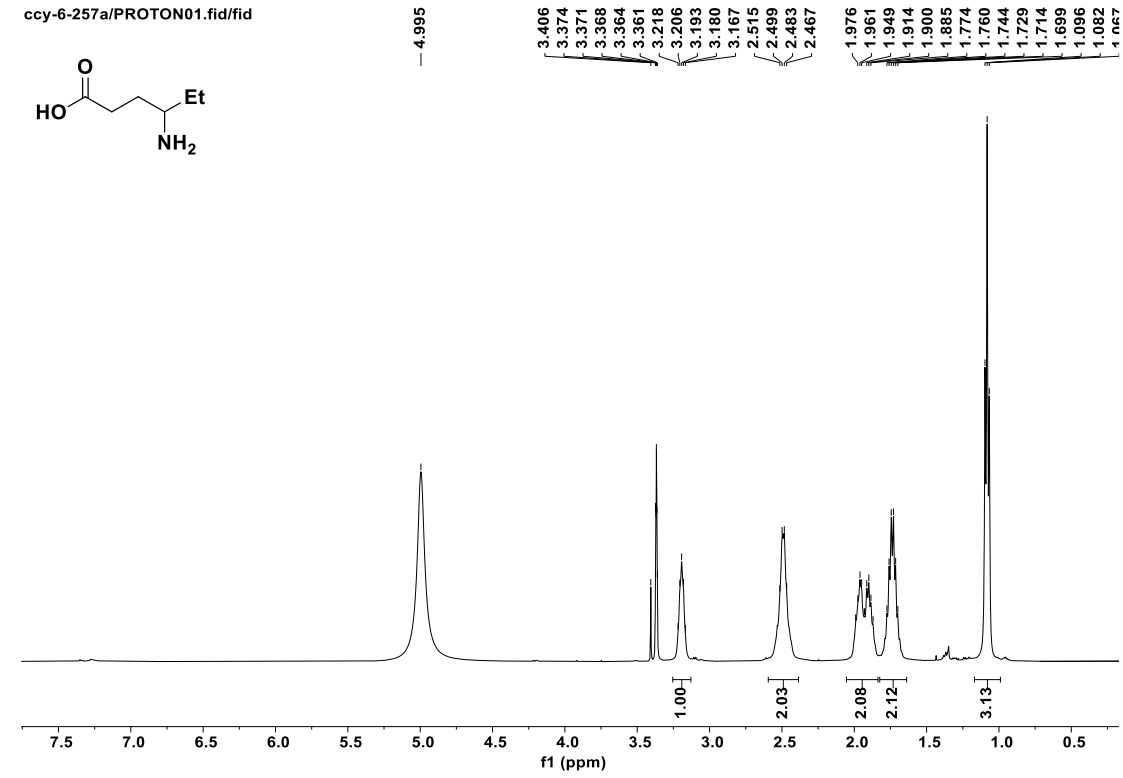

ccy-6-213/3/fid
36.625
35.580
O
Me
CF3
Et2N
P
N
NEt2
Et
O
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

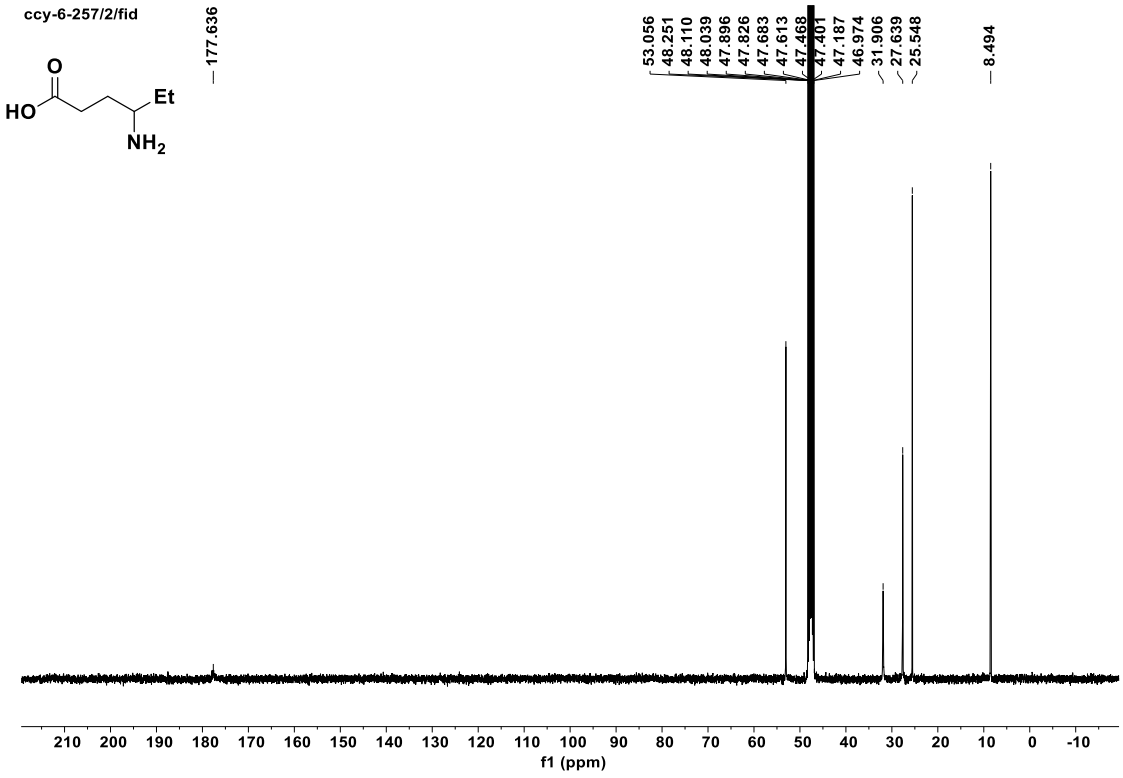

ccy-6-213/FLUORINE01.fid/fid
-62.903
-62.911
O
Me
CF3
Et2N
P
N
NEt2
Et
O
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

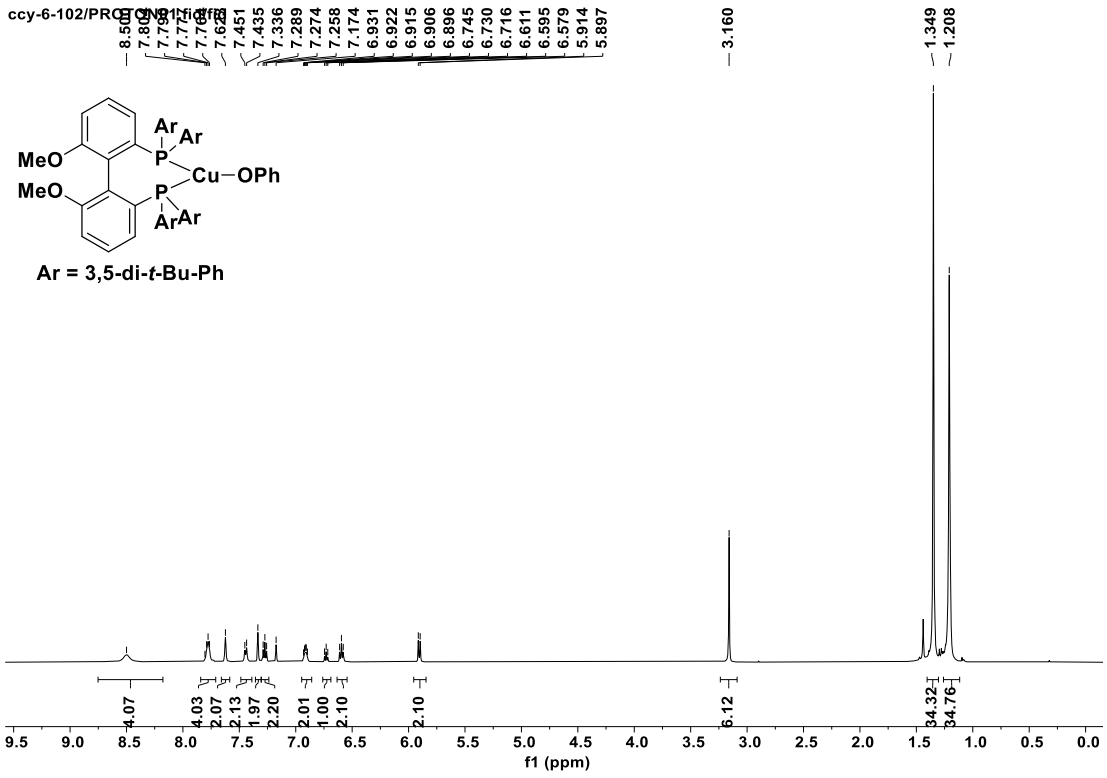

7.636
7.614
7.526
7.507
7.316
7.142
7.132
7.122
7.105
6.711
6.703
6.688
6.514
6.499
3.931
3.904
3.891
3.864
3.407
3.390
3.374
3.124
3.110
3.096
3.035
3.019
3.002
2.640
2.628
2.616
2.604
2.592
1.742
1.739
1.733
1.724
1.718
1.709
1.703
1.695
1.688
1.614
1.608
1.602
1.596
1.592
1.585
1.573
1.570
1.563
1.558
1.543
1.003
0.988
0.973
N
Et
CF3
HN
1.88
1.95
1.88
0.90
0.93
1.92
1.95
2.00
1.99
0.97
2.10
4.02
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

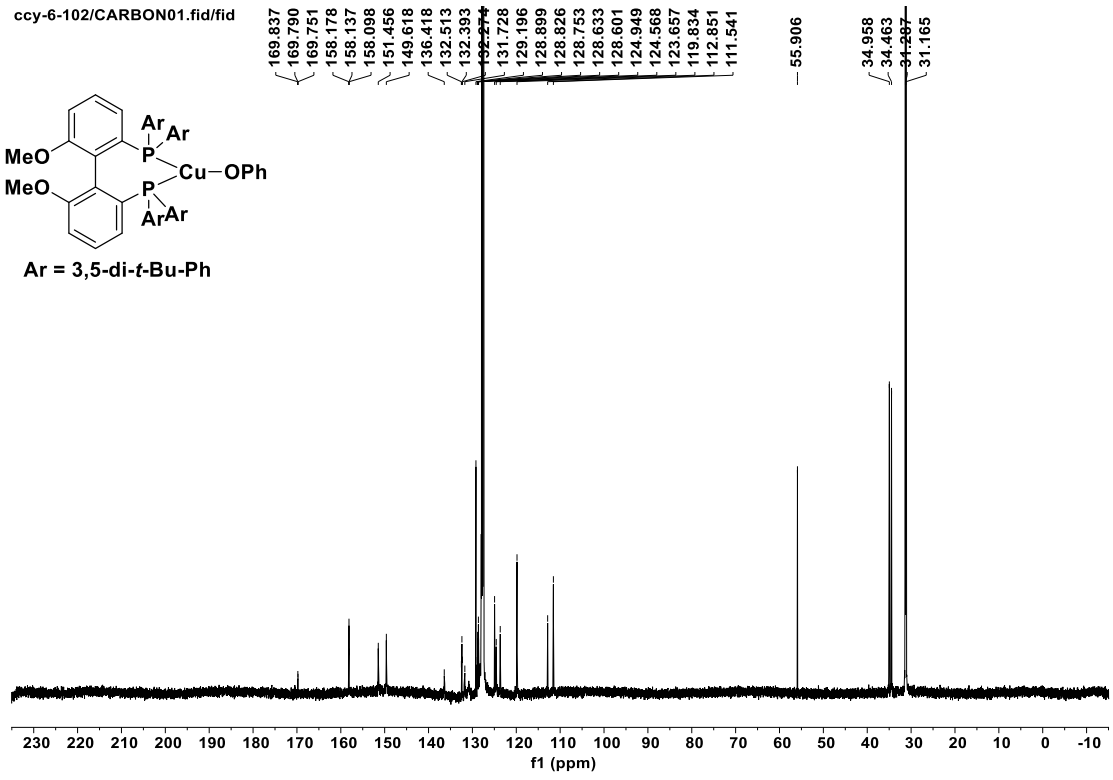

ccy-6-246/1/fid
152.692
145.200
130.015
129.593
129.272
128.951
128.631
128.339
128.306
127.290
126.830
125.655
125.324
125.287
125.249
125.211
124.413
122.954
120.251
117.404
106.873
77.365
77.048
76.730
57.945
53.151
50.560
49.583
30.983
28.584
26.249
23.524
9.798
N
Et
CF3
HN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


ccy-6-246/FLUORINE01.fid/fid
-62.346
N
Et
HN
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


ccy-6-257a/PROTON01.fid/fid
4.995
3.406
3.374
3.371
3.368
3.364
3.361
3.218
3.206
3.193
3.180
3.167
2.515
2.499
2.483
2.467
1.976
1.961
1.949
1.914
1.900
1.885
1.774
1.760
1.744
1.729
1.714
1.699
1.096
1.082
HO
O
Et
NH2
1.00
2.03
2.08
2.12
3.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

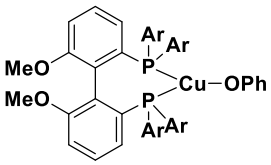

ccy-6-257/2/fid
177.636
53.056
48.251
48.110
48.039
47.896
47.826
47.683
47.613
47.468
47.401
47.187
46.974
31.906
27.639
25.548
8.494
HO
O
Et
NH2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


ccy-6-102/PROTON01.fid/fid
8.500
7.801
7.799
7.772
7.766
7.625
7.451
7.435
7.336
7.289
7.274
7.258
7.174
6.931
6.922
6.915
6.906
6.896
6.745
6.730
6.716
6.611
6.595
6.579
5.914
5.897
3.160
1.349
1.208
Ar Ar
MeO
P
Cu—OPh
MeO
P
Ar Ar
Ar = 3,5-di-t-Bu-Ph
4.07
4.03
2.07
2.13
1.97
2.20
2.01
1.00
2.10
2.10
6.12
34.32
34.76
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

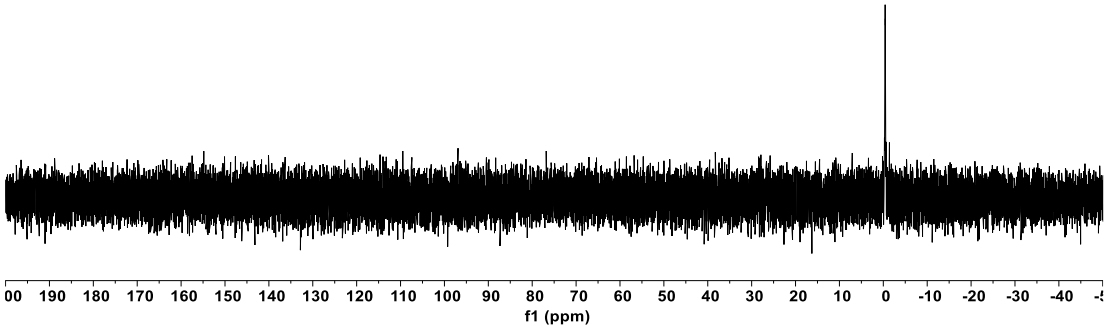

ccy-6-102/CARBON01.fid/fid
169.837
169.790
169.751
158.178
158.137
158.098
151.456
149.618
136.418
132.513
132.393
131.728
129.196
128.899
128.826
128.753
128.633
128.601
124.949
124.568
123.657
119.834
112.851
111.541
55.906
34.958
34.463
31.287
31.165
Ar Ar
MeO
P
Cu—OPh
MeO
P
Ar Ar
Ar = 3,5-di-t-Bu-Ph
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

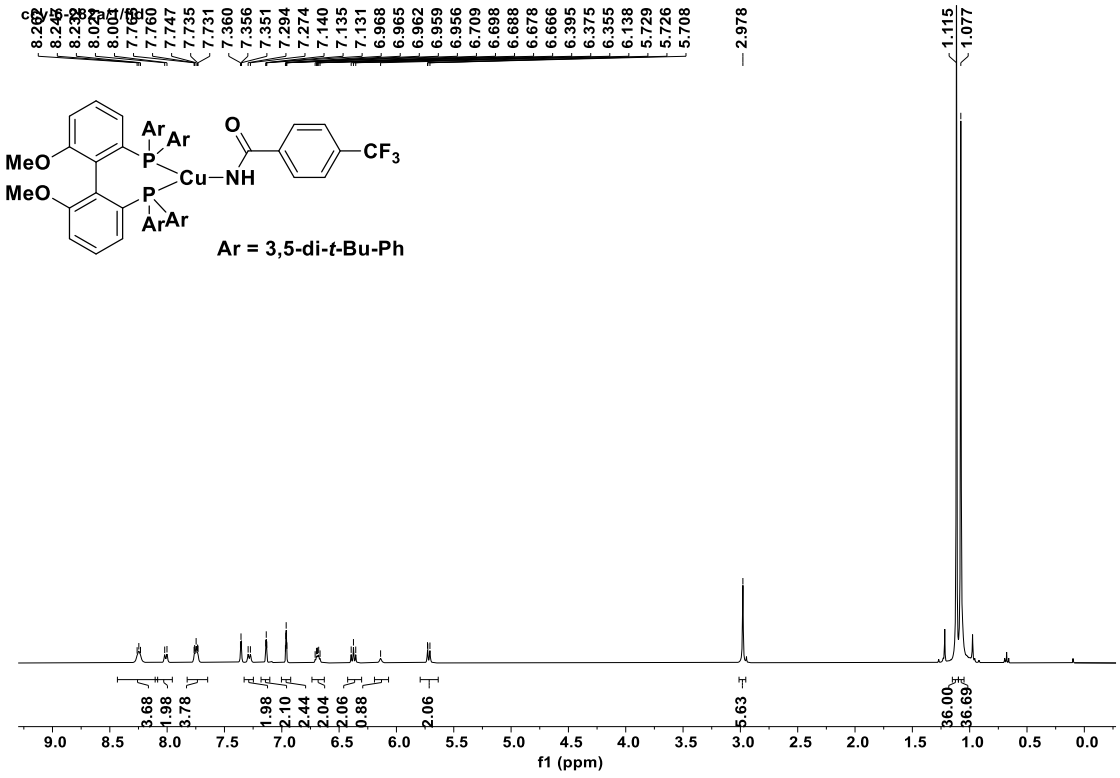
ccy-6-102/PHOSPHORUS01.fid/fid

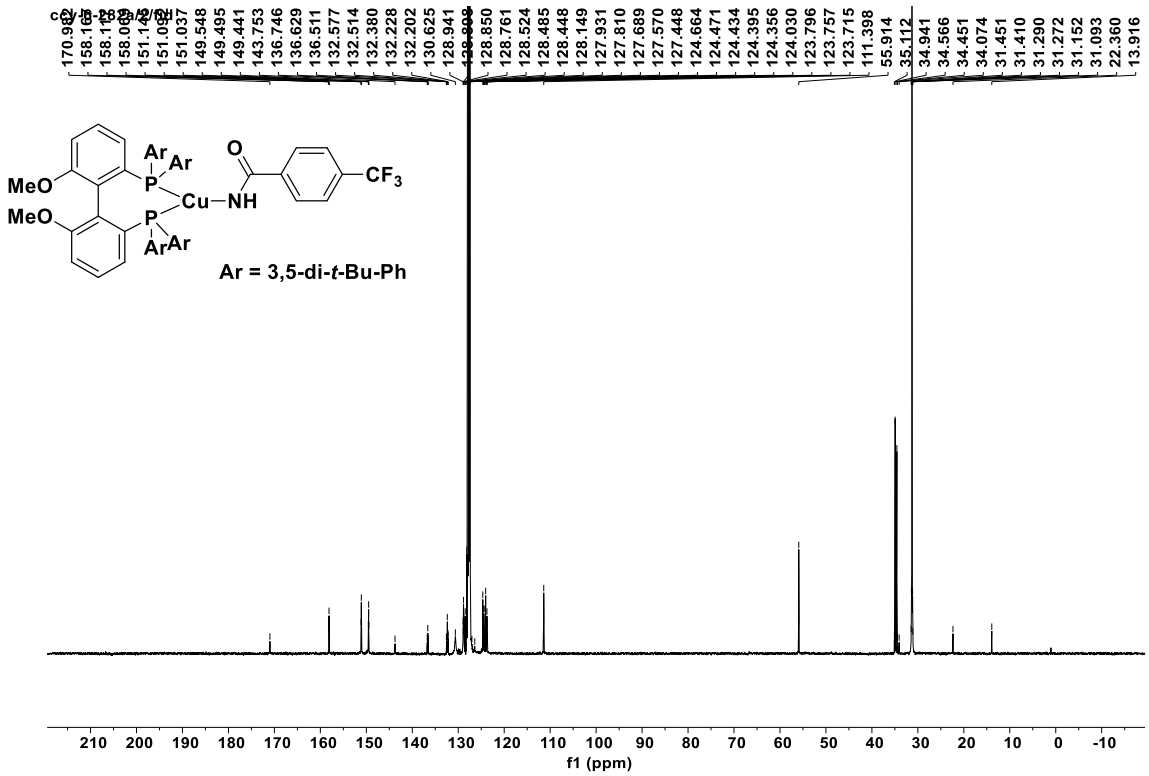
-0.423



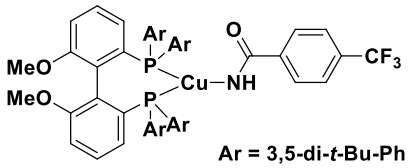
Ar = 3,5-di-*t*-Bu-Ph




MeO
MeO
Ar
Ar
P
Cu
NH
O
CF3
Ar = 3,5-di-t-Bu-Ph
f1 (ppm)

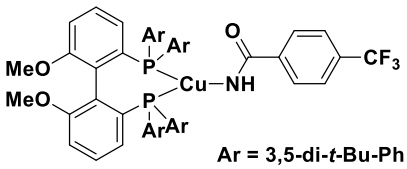

MeO
MeO
Ar
Ar
P
Cu
NH
O
CF3
Ar = 3,5-di-t-Bu-Ph
f1 (ppm)

ccy-6-282a/3/fid

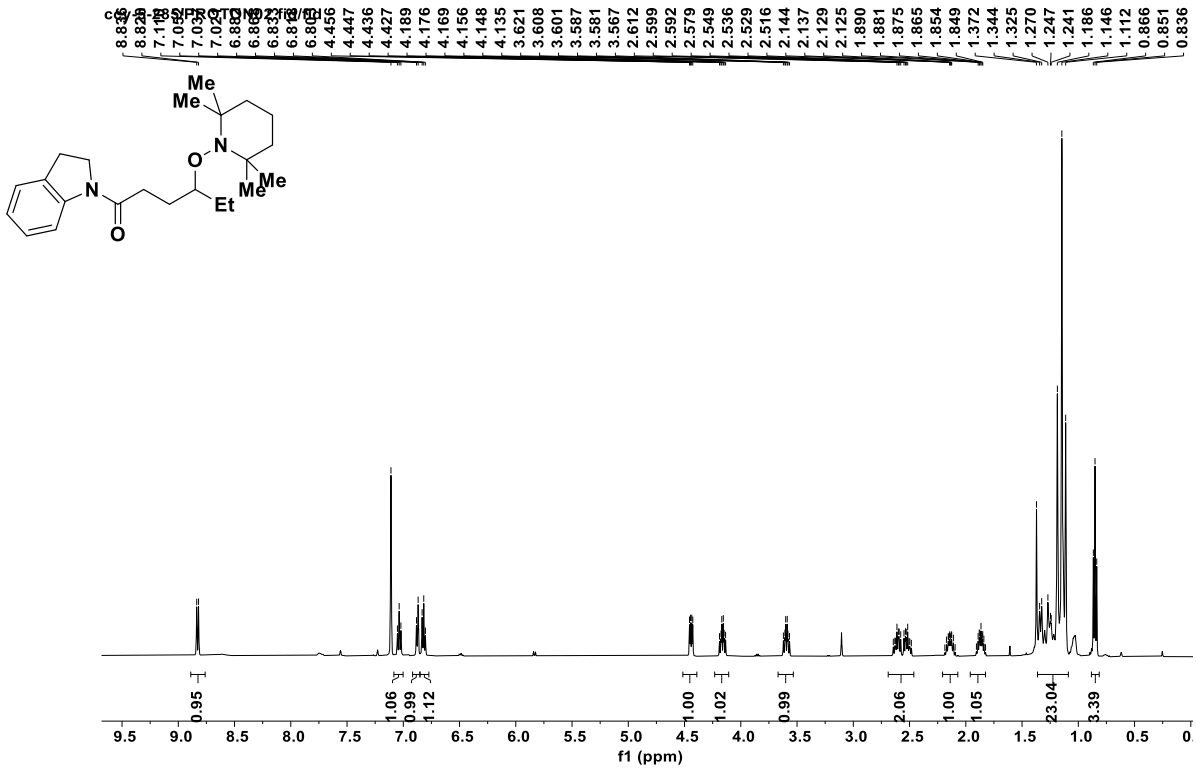


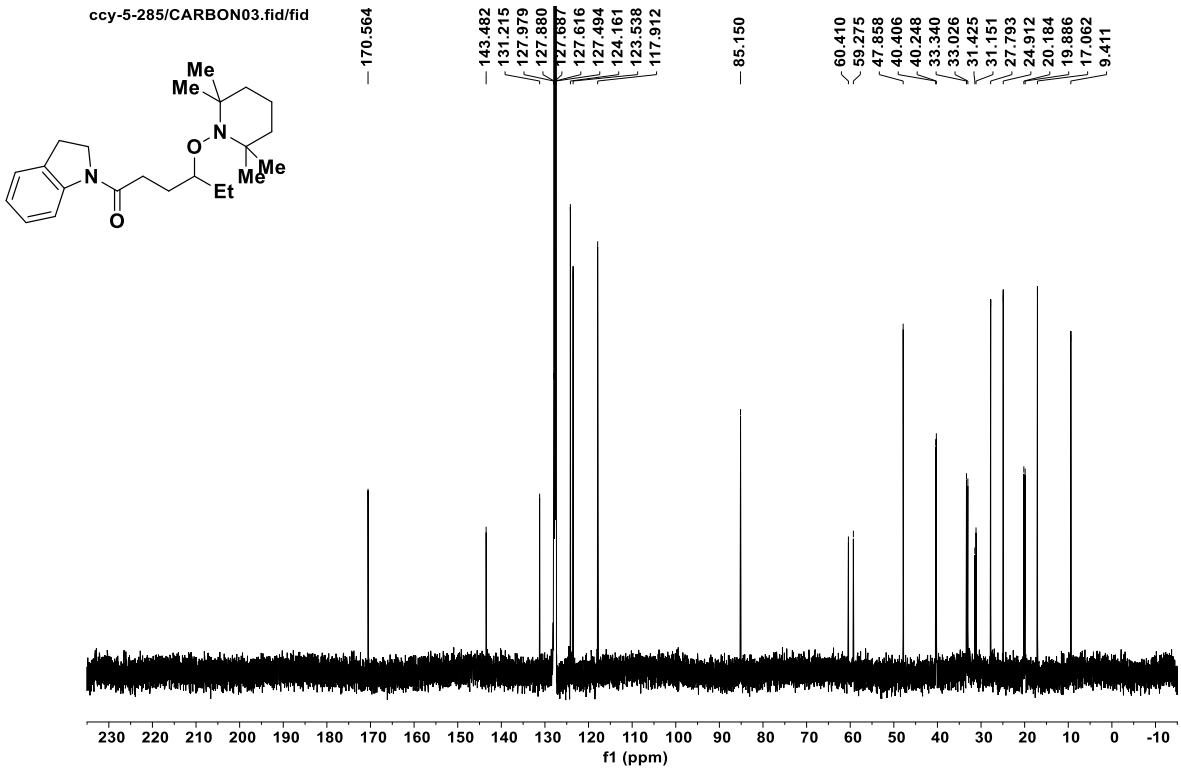
Ar = 3,5-di-*t*-Bu-Ph

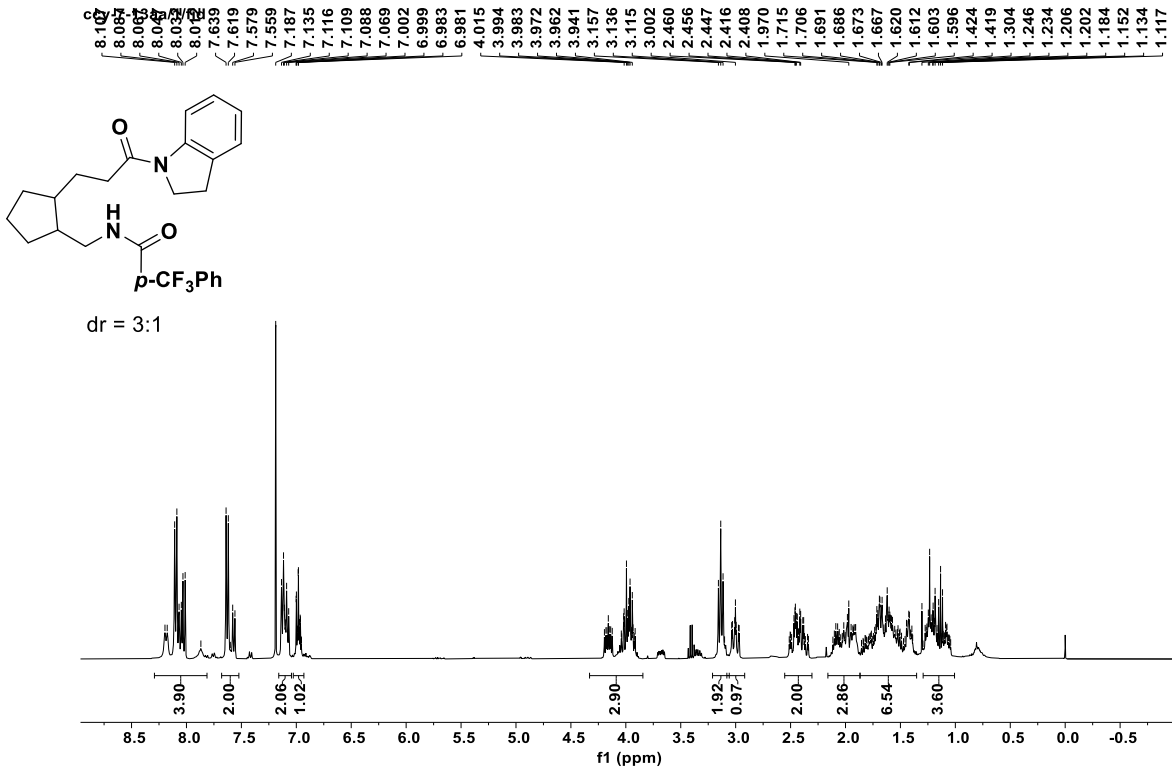
ccy-6-283a/Fluorine.fid

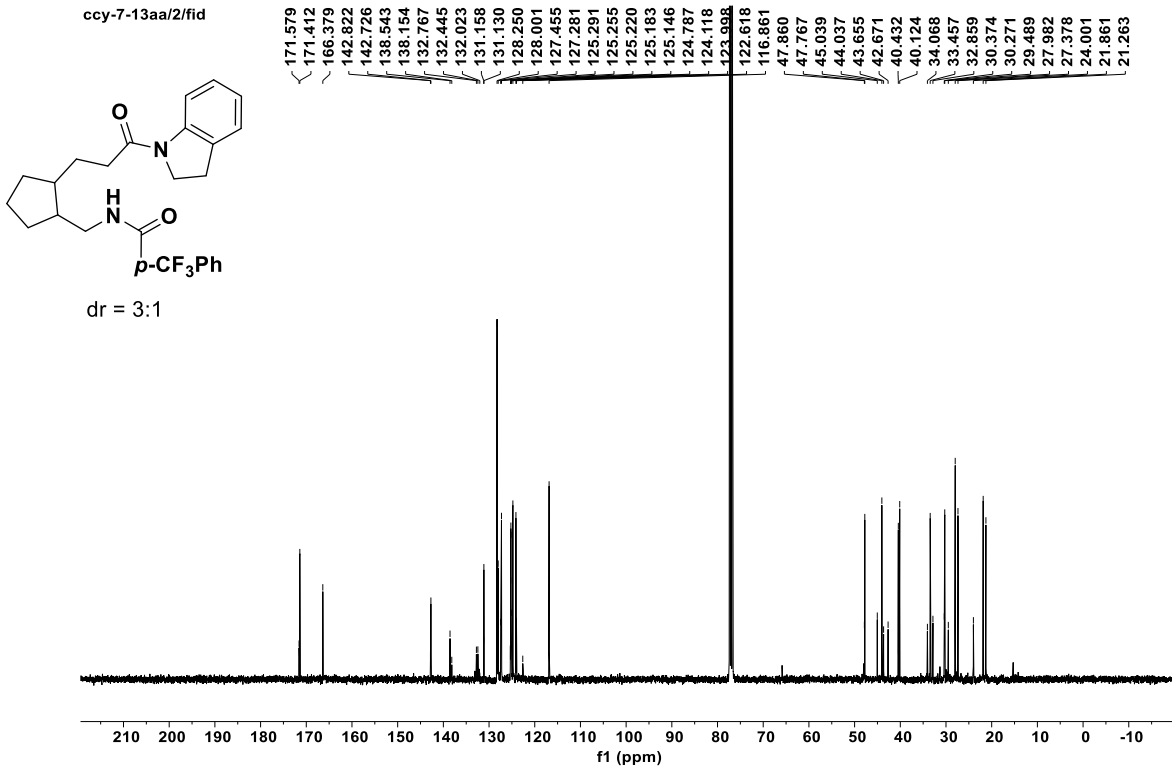


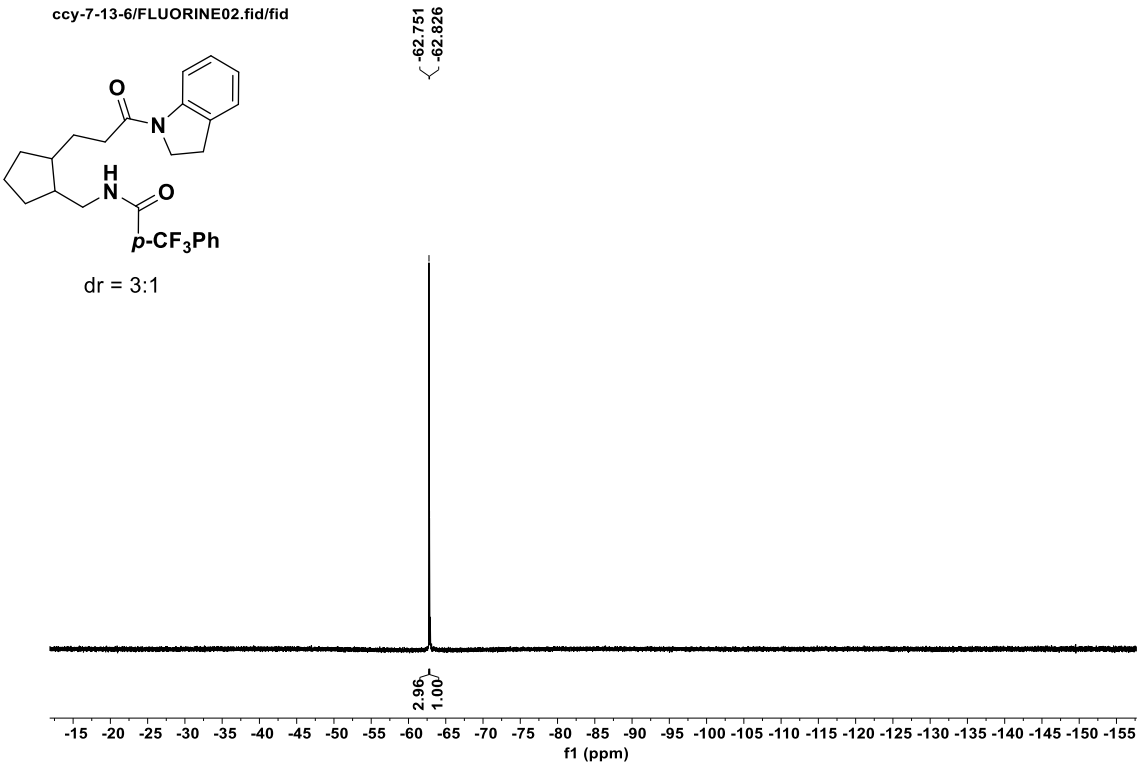
Ar = 3,5-di-*t*-Bu-Ph

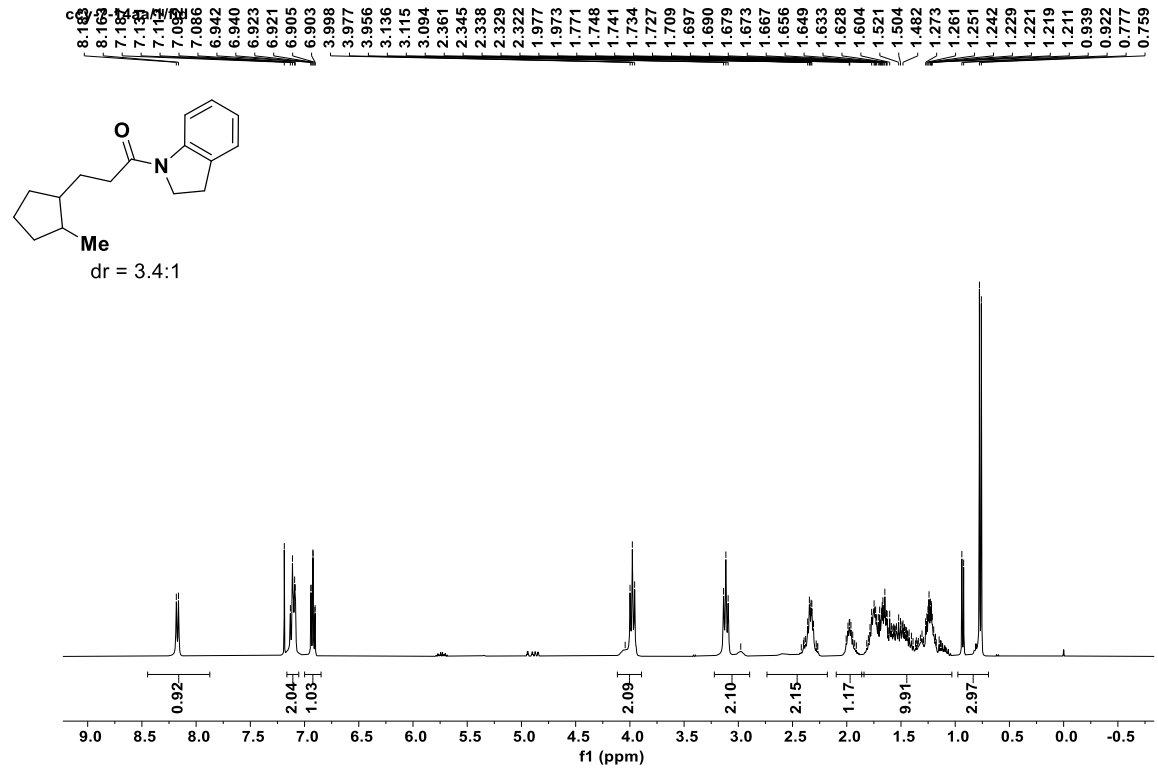

Me
Me
N
O
Me
Me
Et
N
O
0.95
1.06
0.99
1.12
1.00
1.02
0.99
2.06
1.00
1.05
23.04
3.39
f1 (ppm)

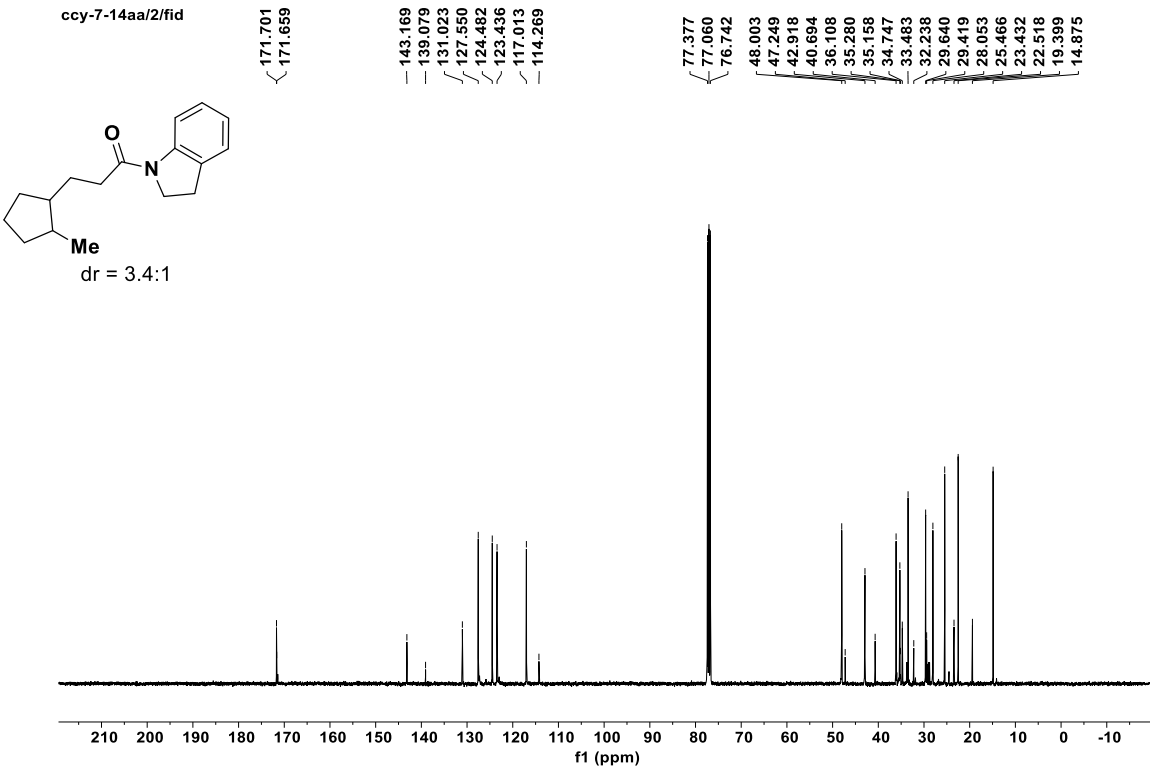

ccy-5-285/CARBON03.fid/fid
170.564
143.482
131.215
127.979
127.880
127.687
127.616
127.494
124.161
123.538
117.912
85.150
60.410
59.275
47.858
40.406
40.248
33.340
33.026
31.425
31.151
27.793
24.912
20.184
19.886
17.062
9.411
Me
Me
N
O
Me
Me
Et
N
O
f1 (ppm)


ccy-7-13aa/1/fid
8.107 8.084 8.067 8.047 8.032 8.012 7.639 7.619 7.579 7.559 7.187 7.135 7.116 7.109 7.088 7.069 7.002 6.999 6.983 6.981 4.015 3.994 3.983 3.972 3.962 3.941 3.157 3.136 3.115 3.002 2.460 2.456 2.447 2.416 2.408 1.970 1.715 1.706 1.691 1.686 1.673 1.667 1.620 1.612 1.603 1.596 1.424 1.419 1.304 1.246 1.234 1.206 1.202 1.184 1.152 1.134 1.117
O
N
H
N
O
p-CF3Ph
dr = 3:1
3.90 2.00 2.06 1.02 2.90 1.92 0.97 2.00 2.86 6.54 3.60
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

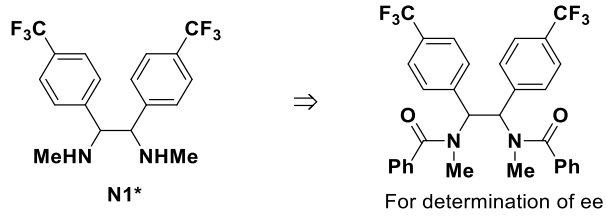

ccy-7-13aa/2/fid
171.579 171.412 166.379 142.822 142.726 138.543 138.154 132.767 132.445 132.023 131.158 131.130 128.250 128.001 127.455 127.281 125.291 125.255 125.220 125.183 125.146 124.787 124.118 123.998 122.618 116.861 47.860 47.767 45.039 44.037 43.655 42.671 40.432 40.124 34.068 33.457 32.859 30.374 30.271 29.489 27.982 27.378 24.001 21.861 21.263
O
N
H
N
O
p-CF3Ph
dr = 3:1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


ccy-7-13-6/FLUORINE02.fid/fid
-62.751
-62.826
O
N
H
N
O
p-CF3Ph
dr = 3:1
2.96
1.00
-15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
f1 (ppm)

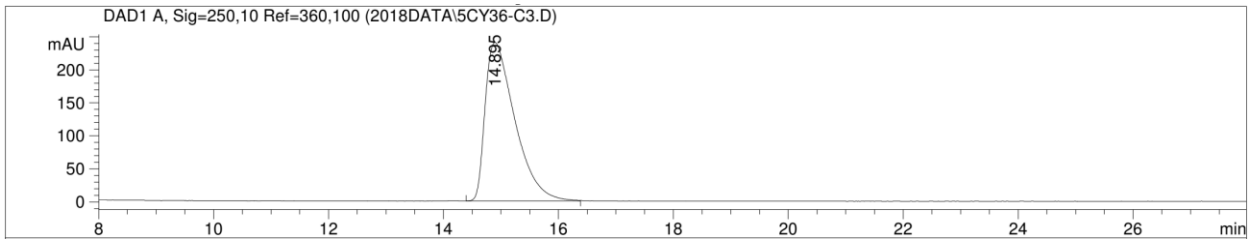

ccy-7-14aa/1/fid
8.162 8.160 7.185 7.183 7.113 7.111 7.092 7.086 6.942 6.940 6.923 6.921 6.905 6.903 3.998 3.977 3.956 3.136 3.115 3.094 2.361 2.345 2.338 2.329 2.322 1.977 1.973 1.771 1.748 1.741 1.734 1.727 1.709 1.697 1.690 1.679 1.673 1.667 1.656 1.649 1.633 1.628 1.604 1.521 1.504 1.482 1.273 1.261 1.251 1.242 1.229 1.221 1.219 1.211 0.939 0.922 0.777 0.759
O
N
Me
dr = 3.4:1
0.92
2.04
1.03
2.09
2.10
2.15
1.17
9.91
2.97
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


ccy-7-14aa/2/fid
171.701 171.659 143.169 139.079 131.023 127.550 124.482 123.436 117.013 114.269 77.377 77.060 76.742 48.003 47.249 42.918 40.694 36.108 35.280 35.158 34.747 33.483 32.238 29.640 29.419 28.053 25.466 23.432 22.518 19.399 14.875
O
N
Me
dr = 3.4:1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Stereoselectivity Analysis

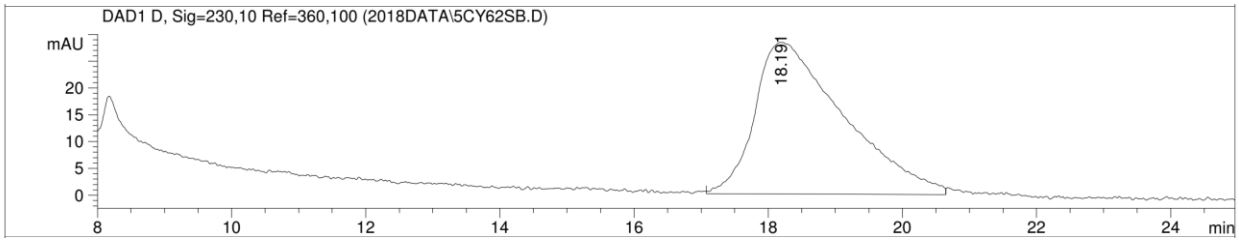


(*S,S*)-**N1*:** >99% ee; (*R,R*)-**N1*:** >99% ee;



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.895	PB	0.5423	8602.42188	239.93622	100.0000



Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.191	BV	1.0875	2610.00879	28.31142	100.0000

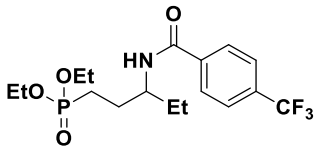
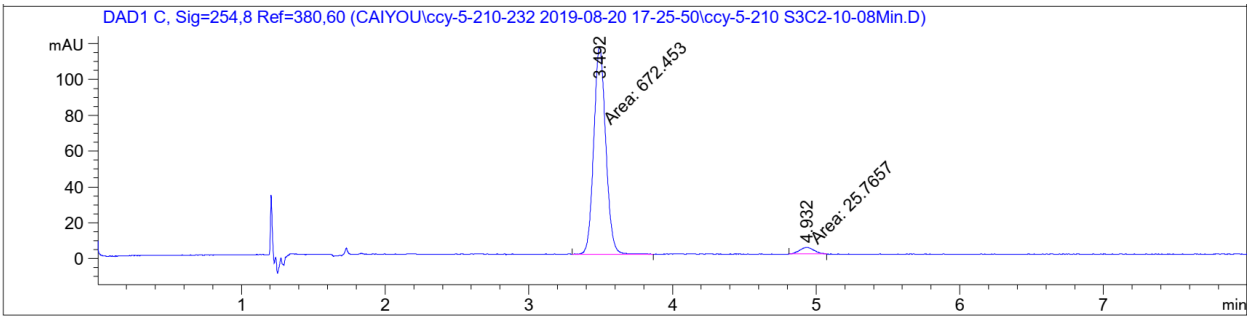
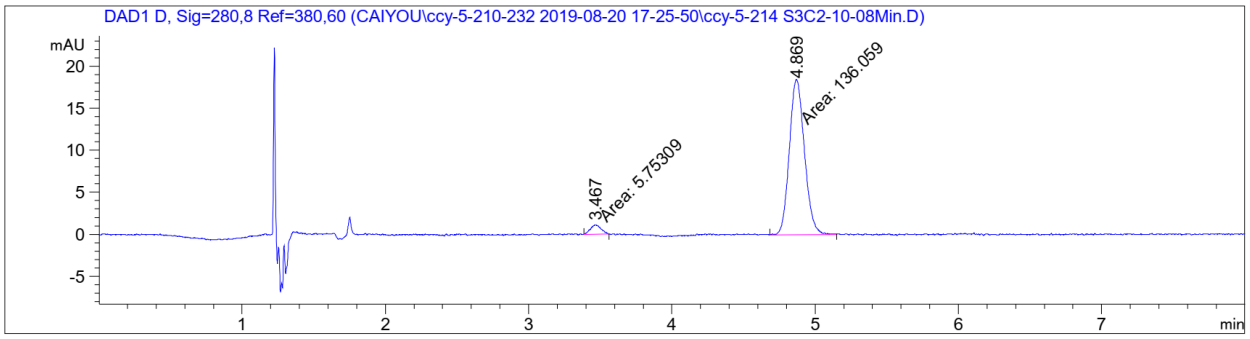


Figure 2, entry 1, (*S,S*)-**N1***: 93% ee; (*R,R*)-**N1***: 92% ee.



Signal 3: DAD1 C, Sig=254,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.492	MM	0.0970	672.45294	115.57478	96.3098
2	4.932	MM	0.1153	25.76573	3.72465	3.6902



Signal 4: DAD1 D, Sig=280,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.467	MM	0.0862	5.75309	1.11248	4.0568
2	4.869	MM	0.1226	136.05949	18.49969	95.9432

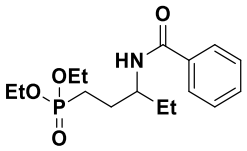
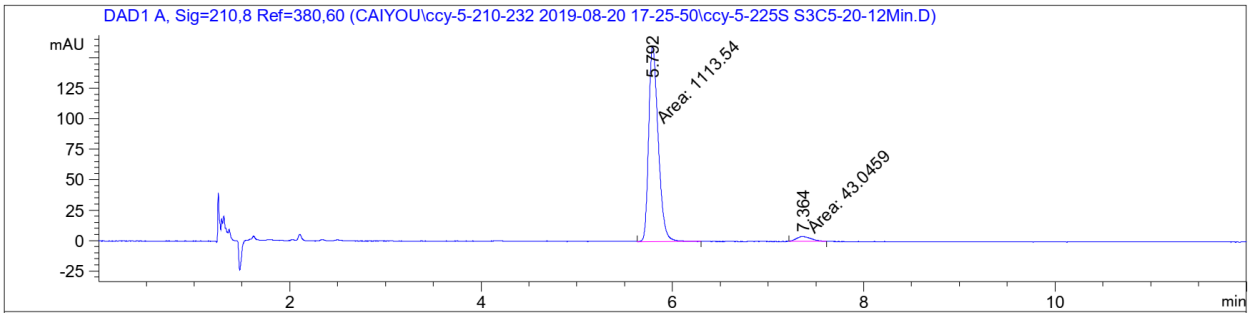
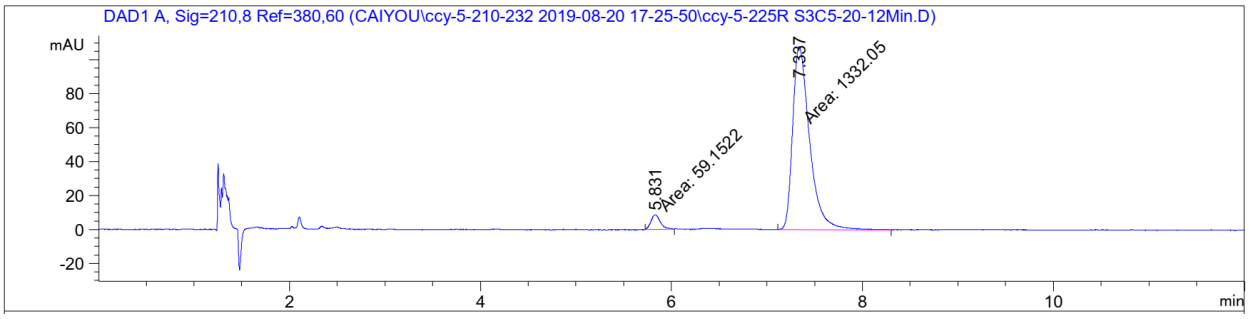


Figure 2, entry 2, (*S,S*)-**N1***: 93% ee; (*R,R*)-**N1***: 92% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.792	MM	0.1155	1113.53601	160.61476	96.2782
2	7.364	MM	0.1797	43.04589	3.99167	3.7218



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.831	MM	0.1141	59.15221	8.64213	4.2519
2	7.337	MM	0.2058	1332.05237	107.87954	95.7481

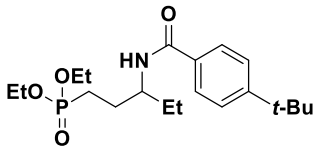
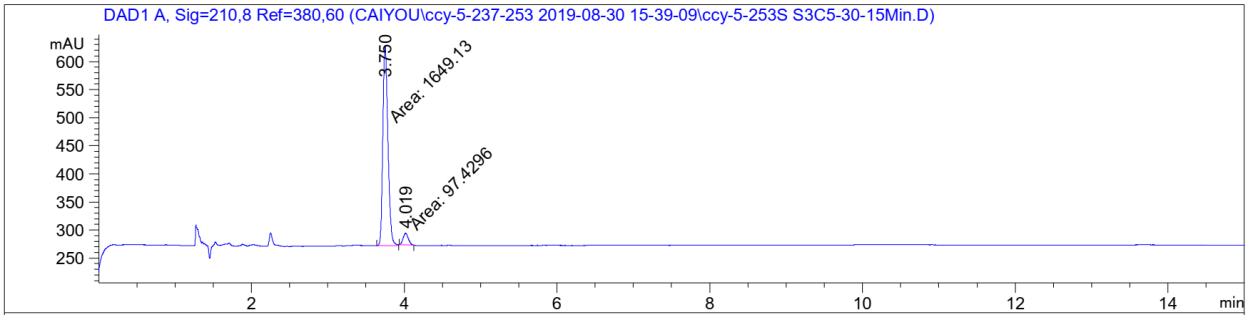
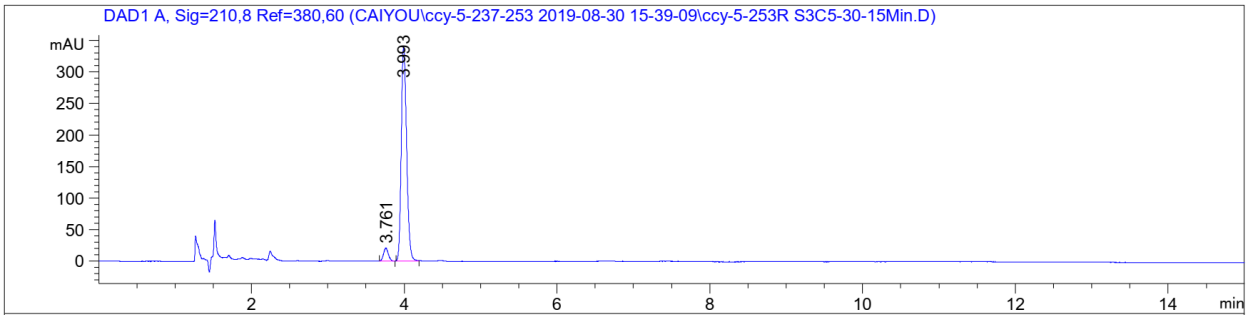


Figure 2, entry 3, (*S,S*)-**N1***: 89% ee; (*R,R*)-**N1***: 90% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.750	MM	0.0771	1649.12634	356.48752	94.4216
2	4.019	MM	0.0791	97.42963	20.53985	5.5784



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.761	BB	0.0694	91.21667	20.70584	5.2123
2	3.993	BB	0.0758	1658.79797	340.63629	94.7877

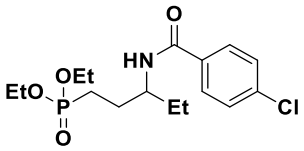
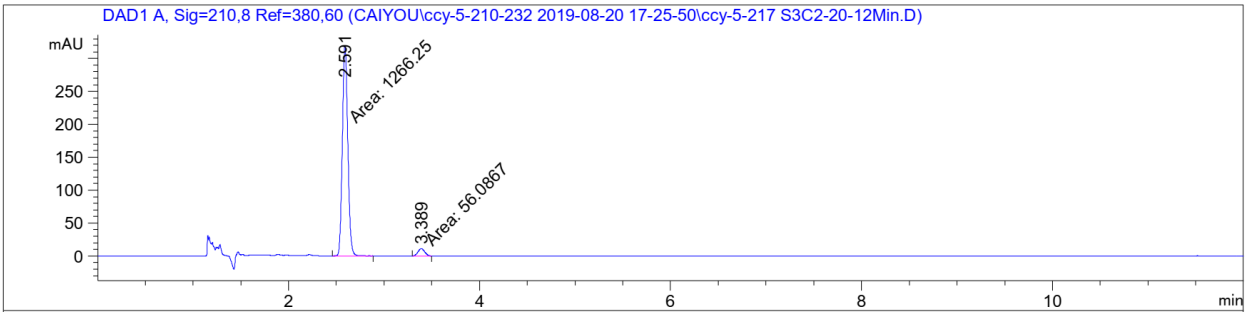
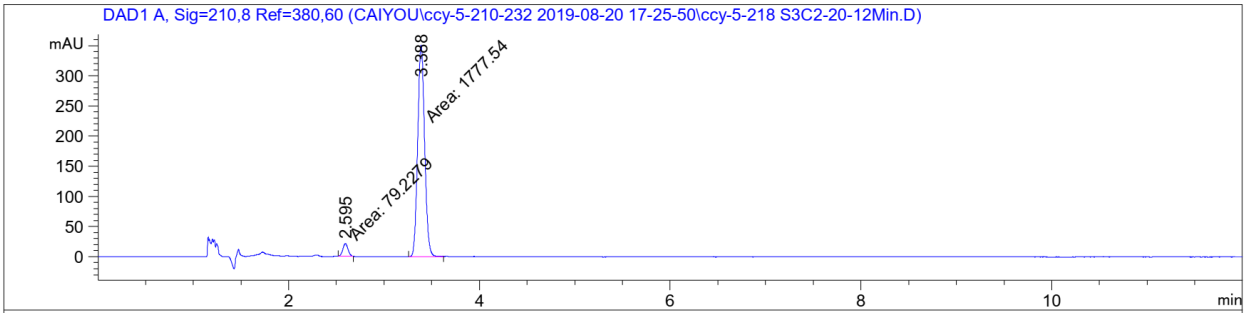


Figure 2, entry 4, (*S,S*)-**N1***: 92% ee; (*R,R*)-**N1***: 92% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.591	MM	0.0660	1266.24866	319.66348	95.7585
2	3.389	MM	0.0831	56.08673	11.24788	4.2415



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.595	MM	0.0630	79.22789	20.96004	4.2670
2	3.388	MM	0.0844	1777.54163	351.01279	95.7330

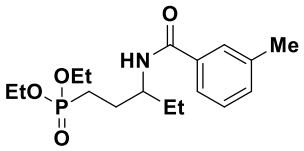
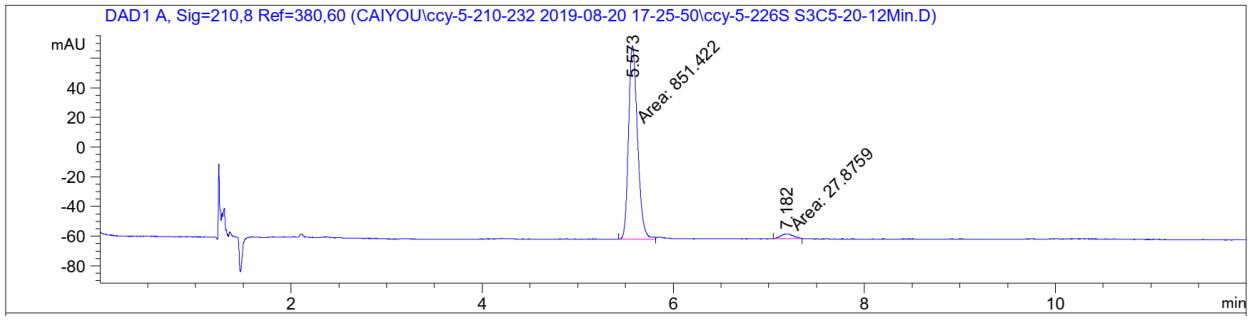
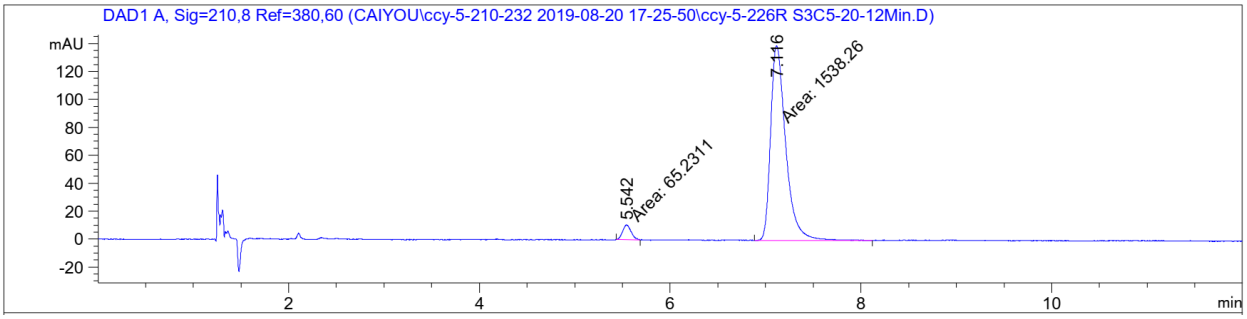


Figure 2, entry 5, (*S,S*)-**N1***: 94% ee; (*R,R*)-**N1***: 92% ee



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.573	MF	0.1091	851.42236	130.07866	96.8298
2	7.182	MM	0.1490	27.87590	3.11904	3.1702



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.542	MM	0.1026	65.23112	10.59602	4.0681
2	7.116	MM	0.1839	1538.25562	139.39607	95.9319

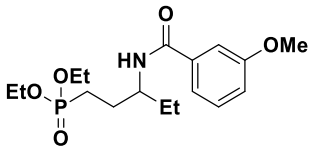
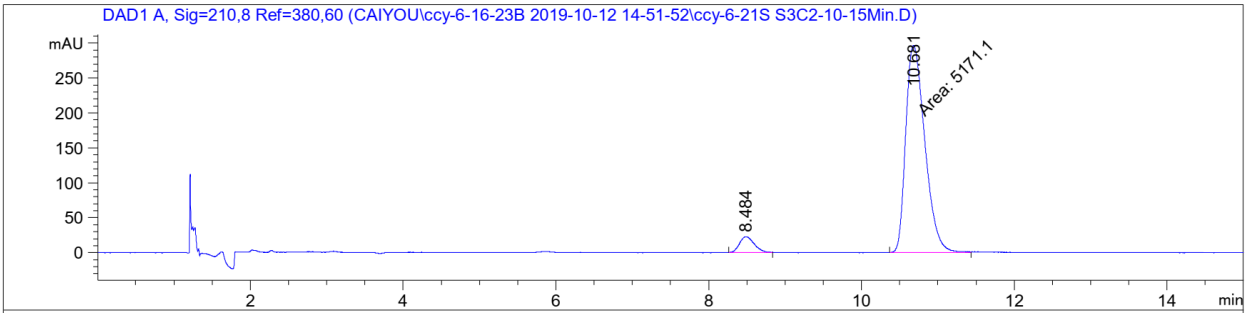
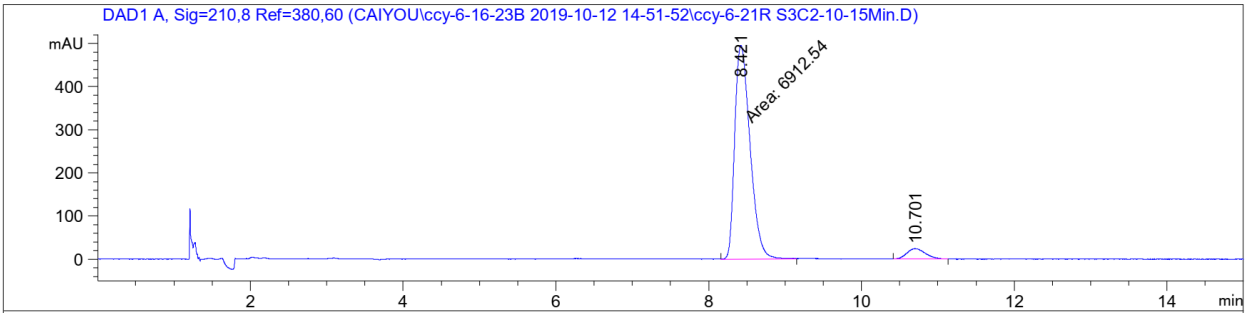


Figure 2, entry 6, (*S,S*)-**N1***: 89% ee; (*R,R*)-**N1***: 89% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.484	BB	0.1702	305.58630	22.82506	5.5798
2	10.681	MM	0.2904	5171.10059	296.73602	94.4202



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.421	MM	0.2325	6912.54492	495.51407	94.4616
2	10.701	BB	0.2000	405.29123	24.00690	5.5384

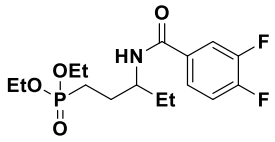
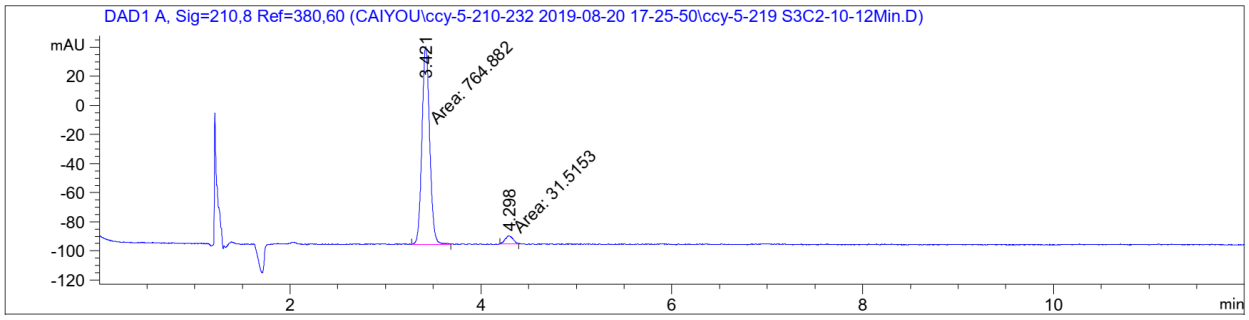
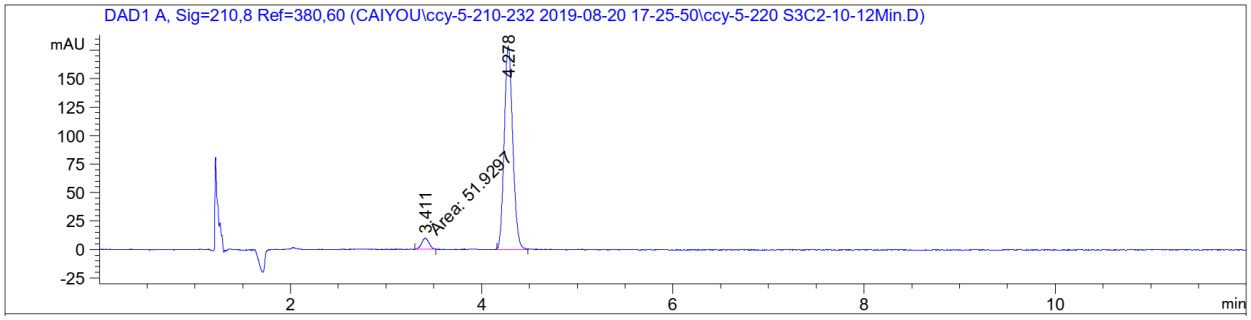


Figure 2, entry 7, (*S,S*)-**N1***: 92% ee; (*R,R*)-**N1***: 91% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.421	MM	0.0938	764.88190	135.91946	96.0428
2	4.298	MM	0.0987	31.51532	5.32141	3.9572



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.411	MM	0.0892	51.92974	9.70358	4.4759
2	4.278	BB	0.0953	1108.28467	178.76202	95.5241

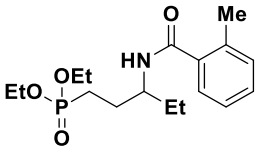
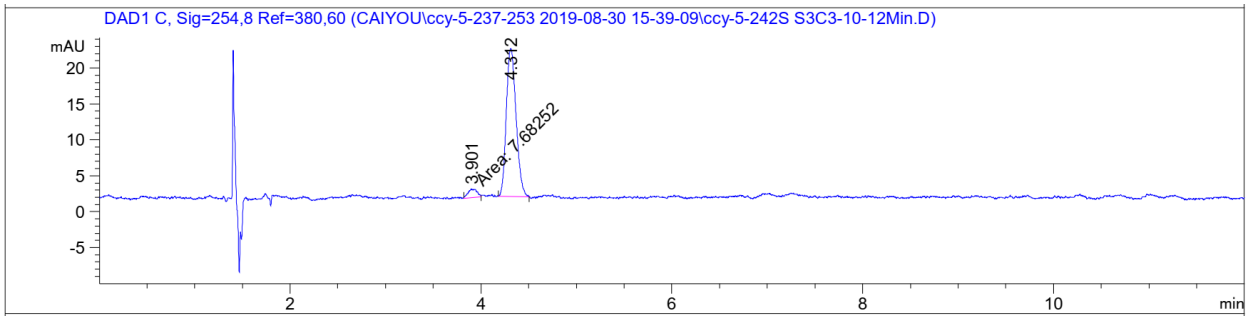
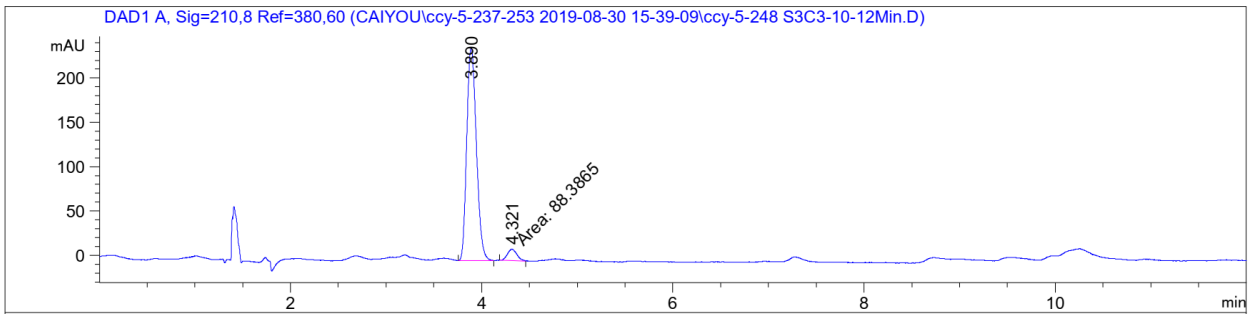


Figure 2, entry 8, (*S,S*)-**N1***: 90% ee; (*R,R*)-**N1***: 90% ee.



Signal 3: DAD1 C, Sig=254,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.901	MM	0.1060	7.68252	1.20842	5.0045
2	4.312	BB	0.1057	145.82925	20.57816	94.9955



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.890	BB	0.1105	1681.17639	240.56641	95.0052
2	4.321	MM	0.1149	88.38651	12.82176	4.9948

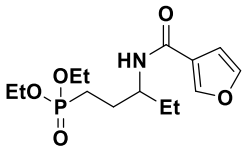
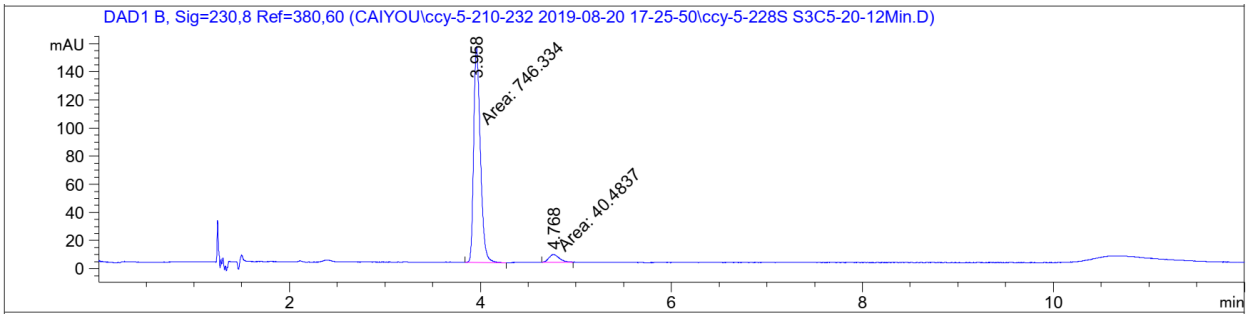
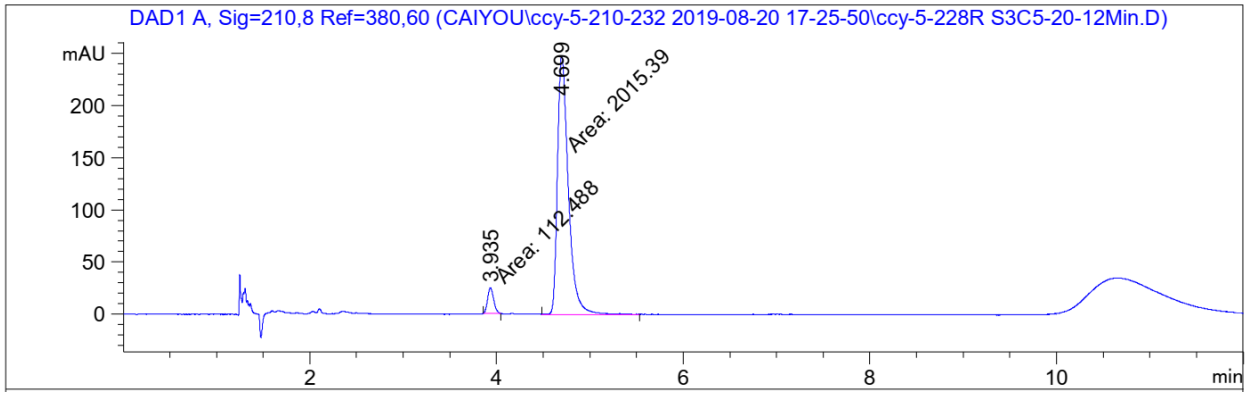


Figure 2, entry 9, (*S,S*)-**N1***: 90% ee; (*R,R*)-**N1***: 90% ee.



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.958	MM	0.0811	746.33386	153.43982	94.8547
2	4.768	MM	0.1249	40.48375	5.40043	5.1453



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.935	MM	0.0757	112.48762	24.76906	5.2864
2	4.699	MM	0.1356	2015.38806	247.71175	94.7136

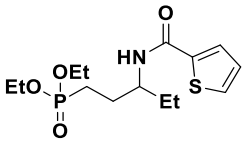
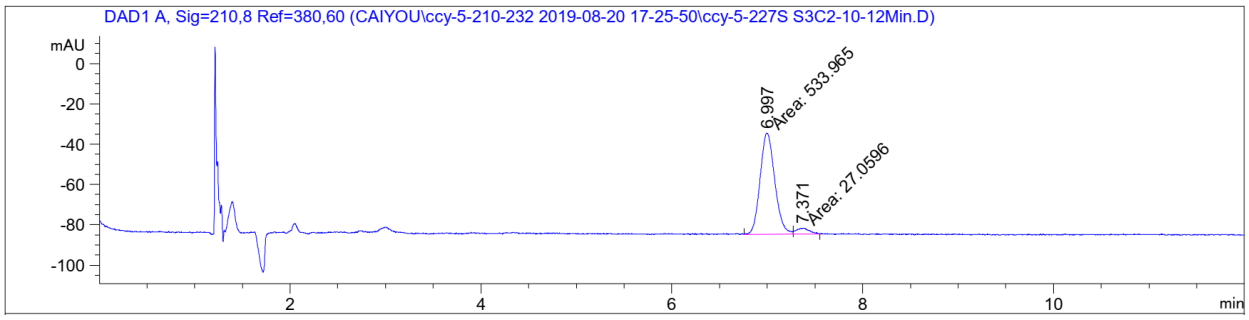
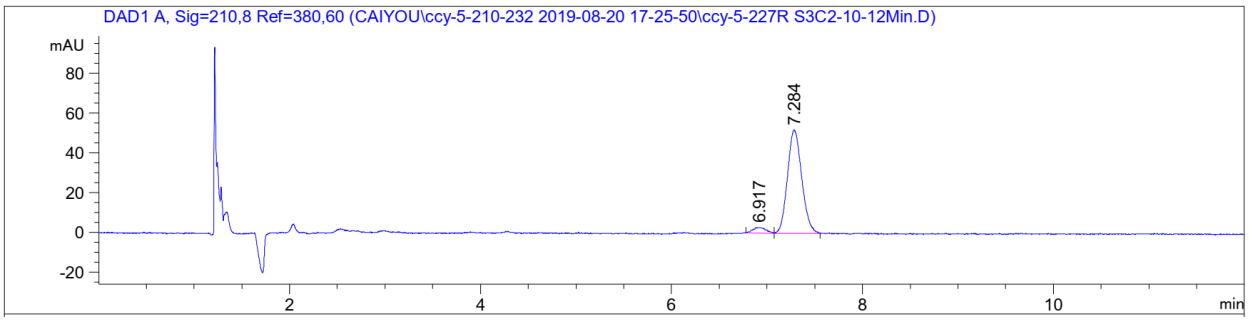


Figure 2, entry 10, (*S*,*S*)-**N1***: 90% ee; (*R*,*R*)-**N1***: 90% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.997	MF	0.1773	533.96478	50.18756	95.1768
2	7.371	FM	0.1564	27.05955	2.88406	4.8232



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.917	BV	0.1149	27.90492	2.91019	4.9193
2	7.284	VB	0.1519	539.35071	52.05153	95.0807

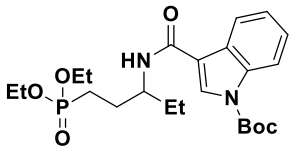
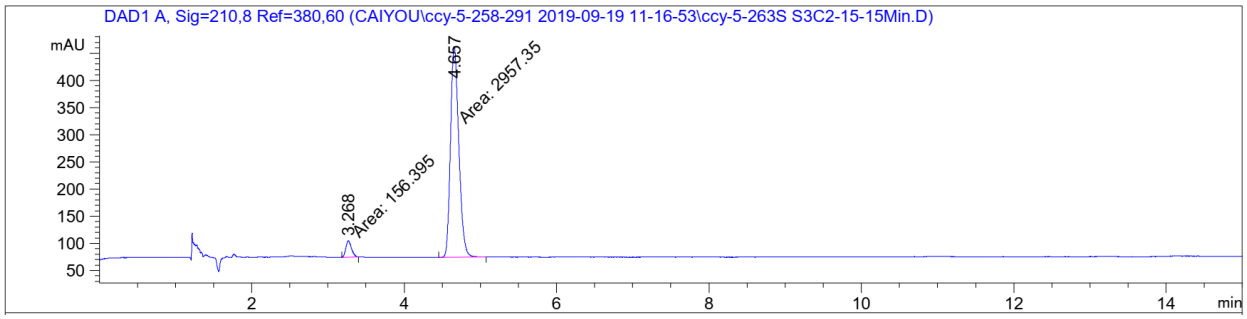
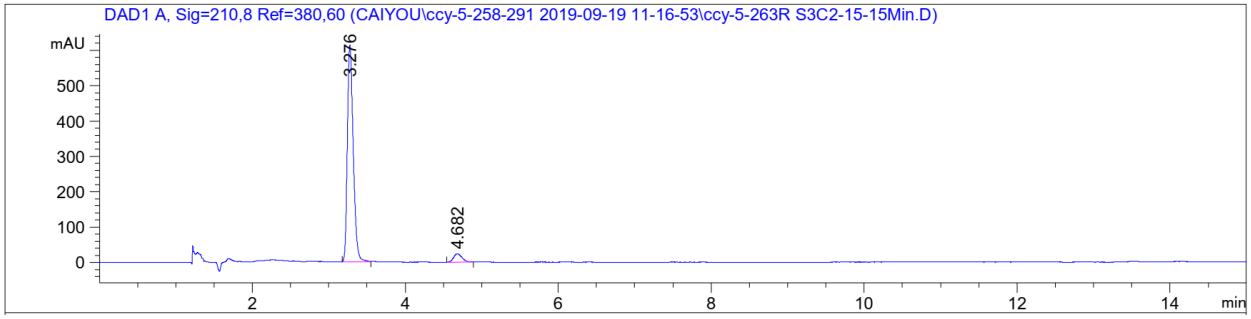


Figure 2, entry 11, (*S,S*)-**N1***: 90% ee; (*R,R*)-**N1***: 90% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.268	MM	0.0858	156.39522	30.37716	5.0227
2	4.657	MM	0.1271	2957.35376	387.87714	94.9773



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.276	BB	0.0822	3268.63281	612.87524	94.8651
2	4.682	BB	0.1113	176.92657	23.64663	5.1349

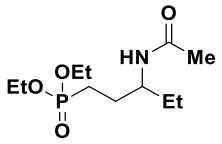
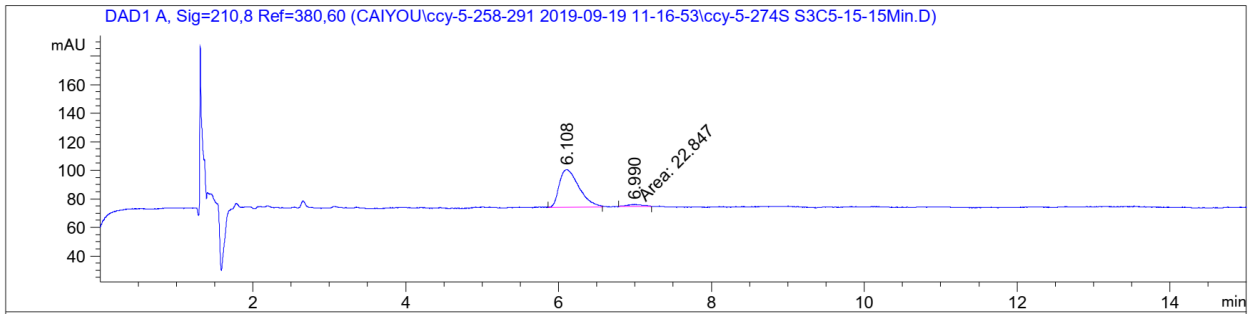
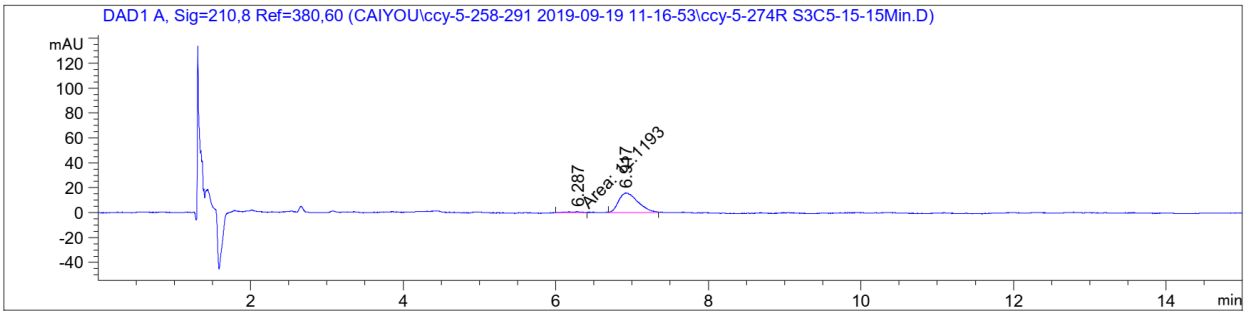


Figure 2, entry 12, (*S*,*S*)-**N1***: 91% ee; (*R*,*R*)-**N1***: 91% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.108	BB	0.2256	467.19498	26.24967	95.3377
2	6.990	MM	0.2531	22.84700	1.50439	4.6623
Totals :				490.04198	27.75406	



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.287	MM	0.2281	12.11929	8.85674e-1	4.2514
2	6.917	BB	0.2078	272.94855	15.62548	95.7486

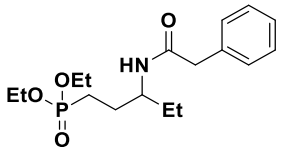
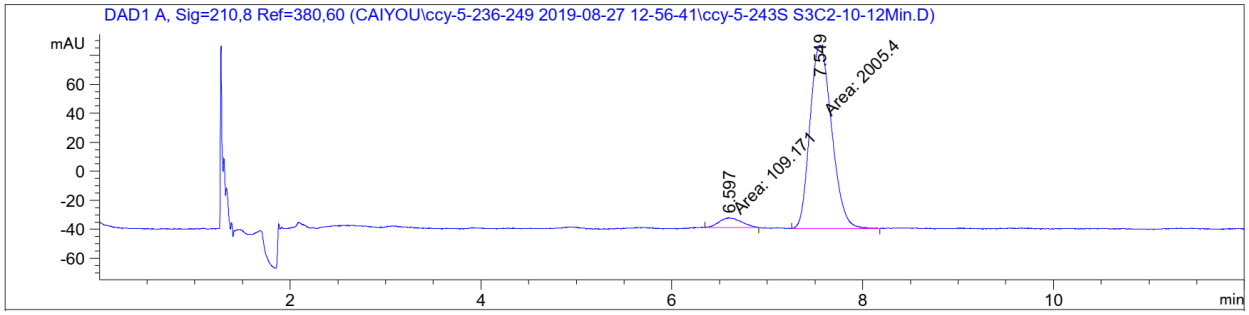
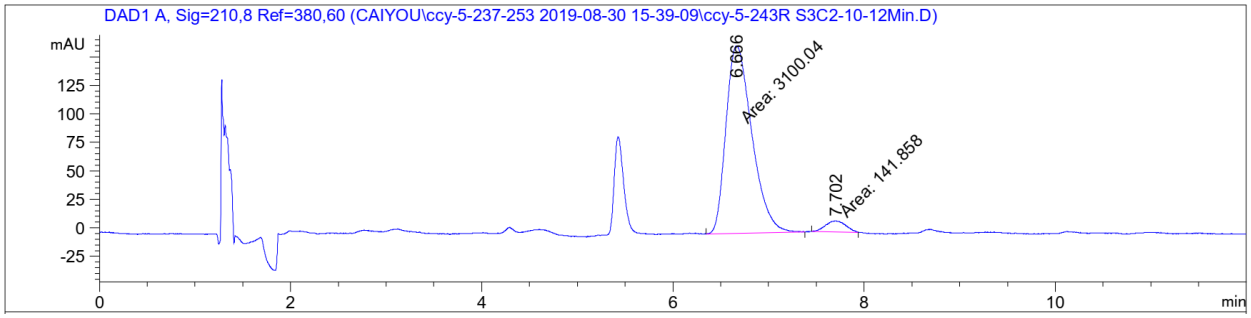


Figure 2, entry 13, (*S,S*)-**N1***: 90% ee; (*R,R*)-**N1***: 91% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.597	MM	0.2709	109.17138	6.71581	5.1628
2	7.549	MM	0.2643	2005.40308	126.46426	94.8372



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.666	MM	0.3140	3100.04395	164.52885	95.6242
2	7.702	MM	0.2493	141.85814	9.48362	4.3758

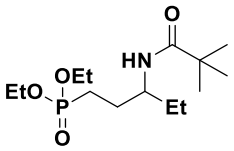
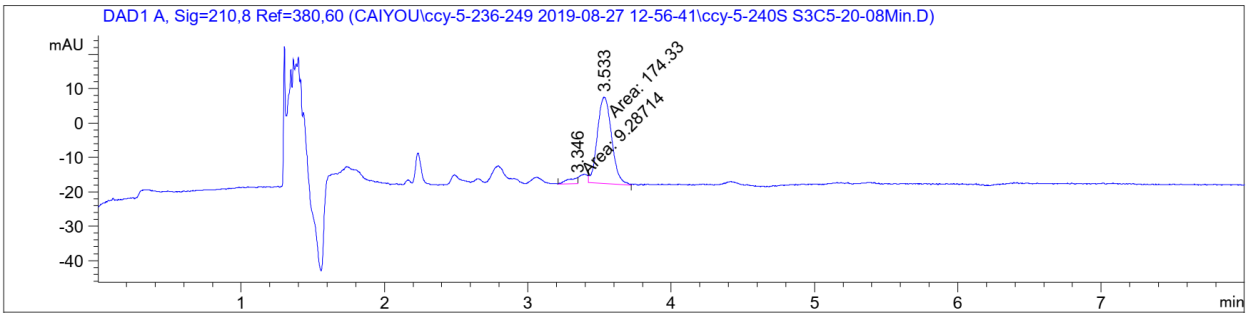
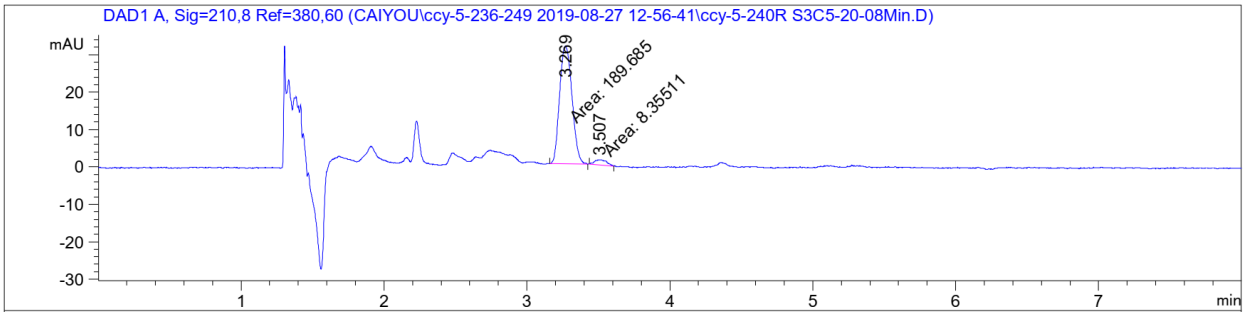


Figure 2, entry 14, (*S,S*)-**N1***: 90% ee; (*R,R*)-**N1***: 91% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.346	MM	0.0850	9.28714	1.82088	5.0579
2	3.533	MM	0.1157	174.32976	25.12205	94.9421



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.269	MM	0.1005	189.68471	31.47028	95.7811
2	3.507	MM	0.0991	8.35511	1.40448	4.2189

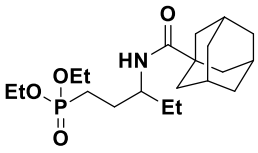
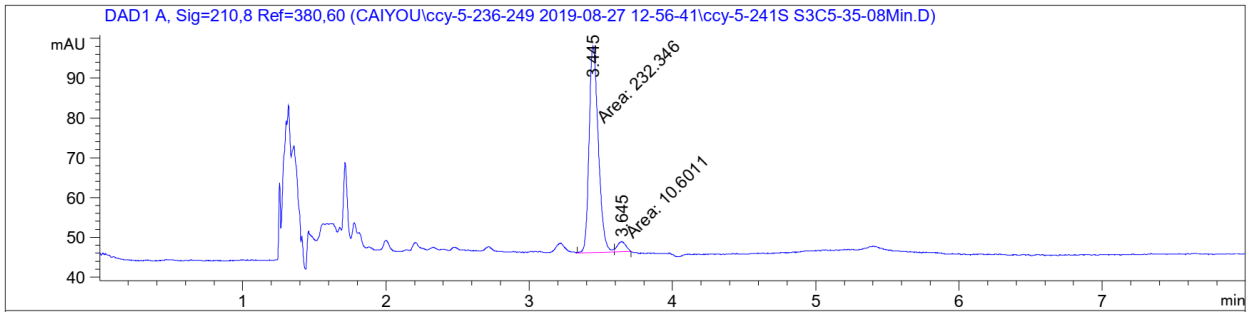
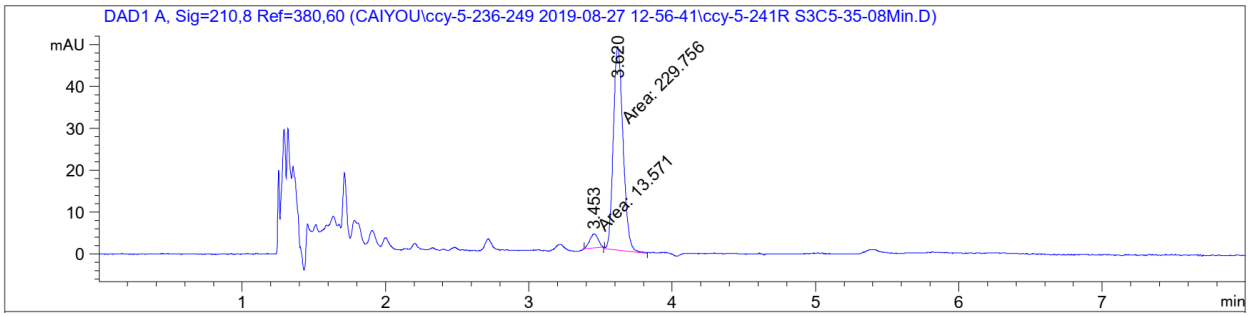


Figure 2, entry 15, (*S,S*)-**N1***: 91% ee; (*R,R*)-**N1***: 89% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.445	MF	0.0745	232.34554	51.96035	95.6364
2	3.645	FM	0.0683	10.60114	2.58609	4.3636



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.453	MM	0.0684	13.57095	3.30838	5.5773
2	3.620	MM	0.0787	229.75577	48.63853	94.4227

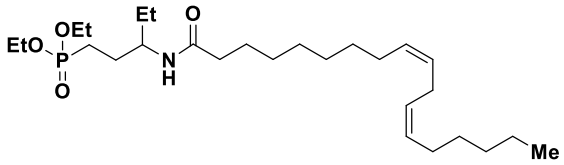
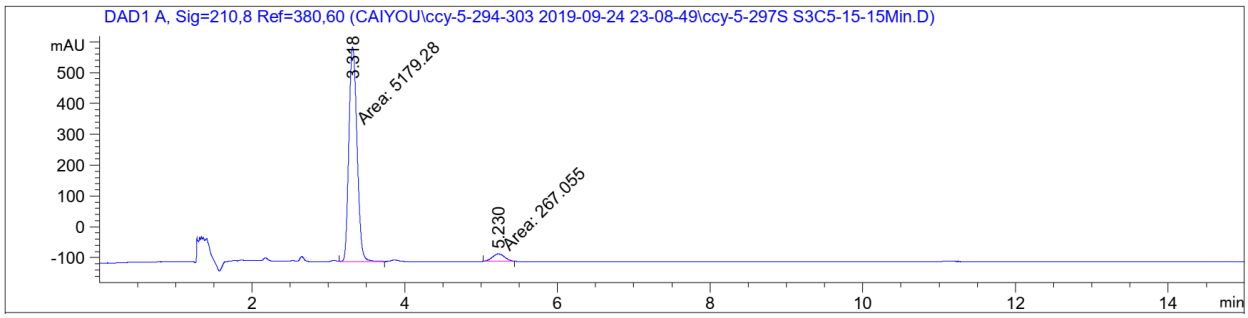
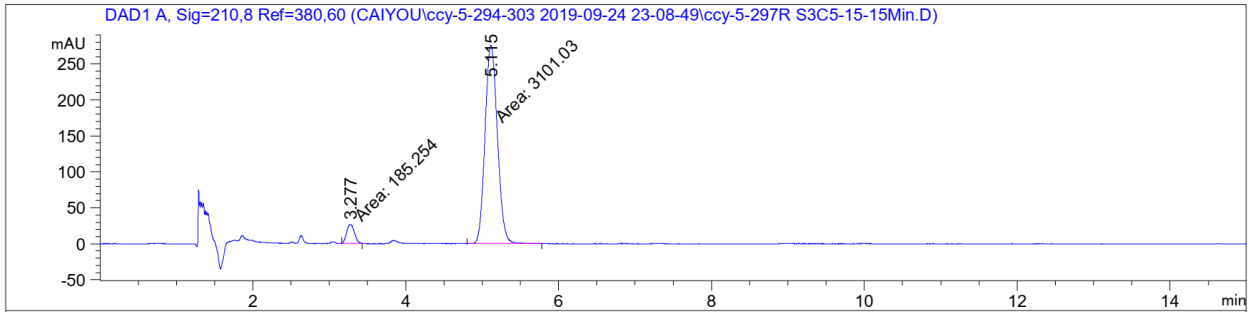


Figure 2, entry 16, (*S,S*)-**N1***: 90% ee; (*R,R*)-**N1***: 89% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.318	MM	0.1240	5179.28076	696.06818	95.0966
2	5.230	MM	0.1866	267.05515	23.85829	4.9034



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.277	MM	0.1171	185.25449	26.36673	5.6372
2	5.115	MM	0.1875	3101.03247	275.67450	94.3628

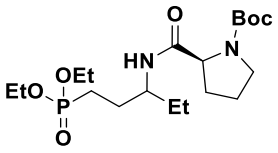
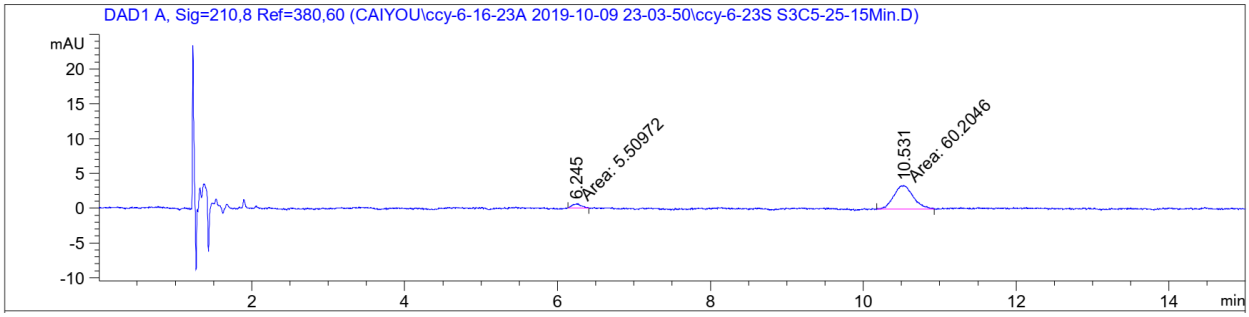
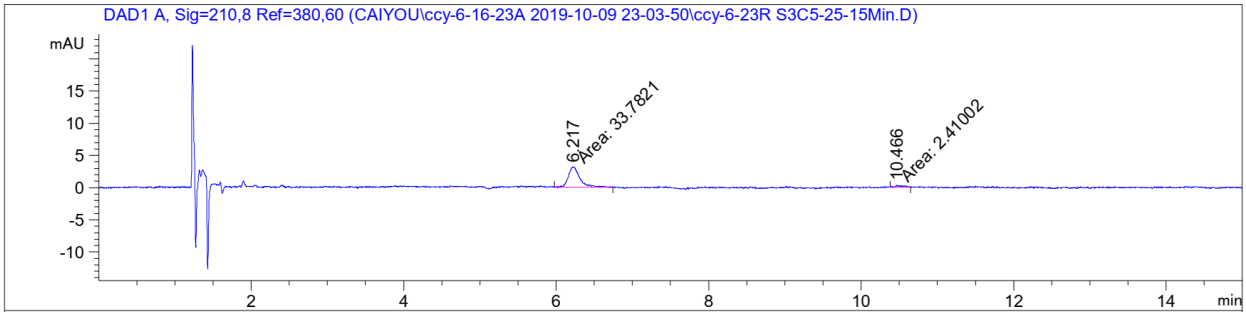


Figure 2, entry 17, (*S,S*)-**N1***: 8:92 dr; (*R,R*)-**N1***: 93:7 dr.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.245	MM	0.1439	5.50972	6.38338e-1	8.3843
2	10.531	MM	0.2944	60.20461	3.40860	91.6157



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.217	MM	0.1791	33.78212	3.14297	93.3410
2	10.466	MM	0.1392	2.41002	2.88521e-1	6.6590

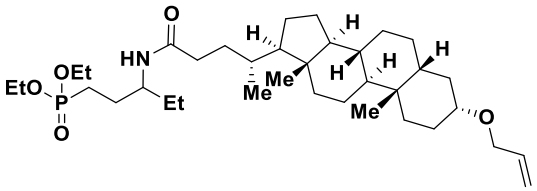
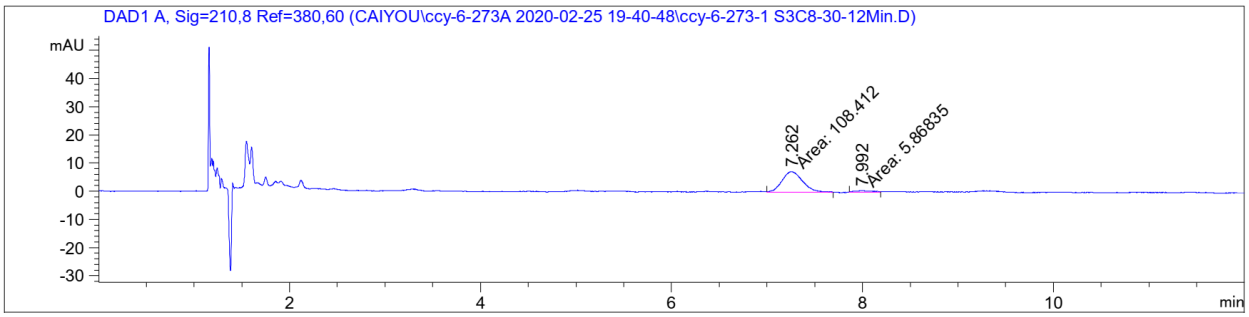
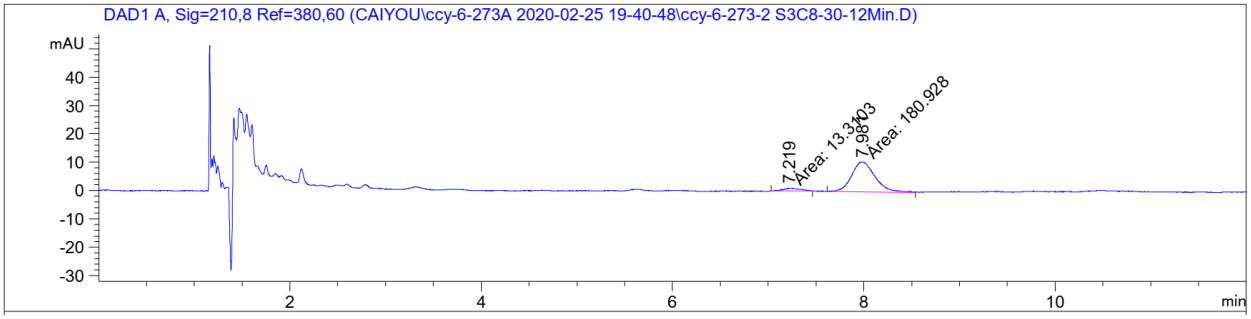


Figure 2, entry 18, (*S,S*)-**N1***: 95:5 dr; (*R,R*)-**N1***: 7:93 dr.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.262	MM	0.2488	108.41212	7.26218	94.8650
2	7.992	MM	0.2113	5.86835	4.62860e-1	5.1350



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.219	MM	0.2222	13.31030	9.98542e-1	6.8526
2	7.981	MM	0.2850	180.92821	10.58216	93.1474

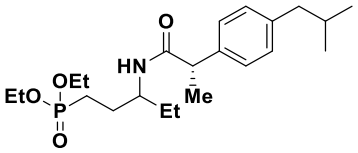
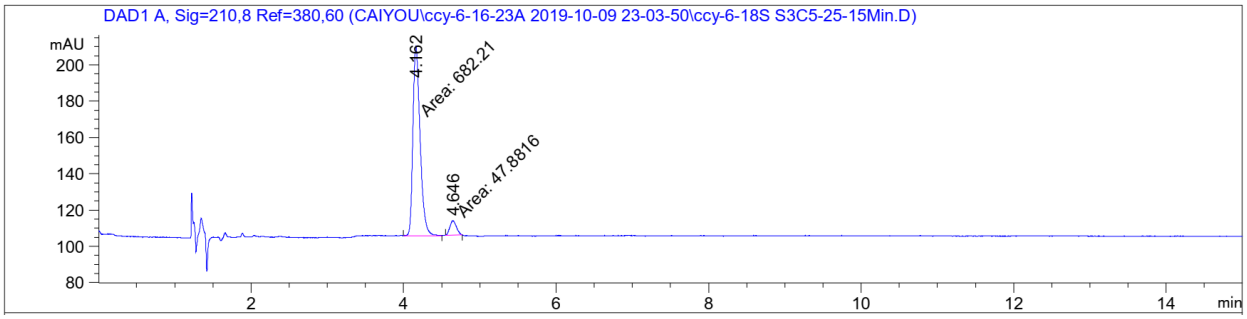
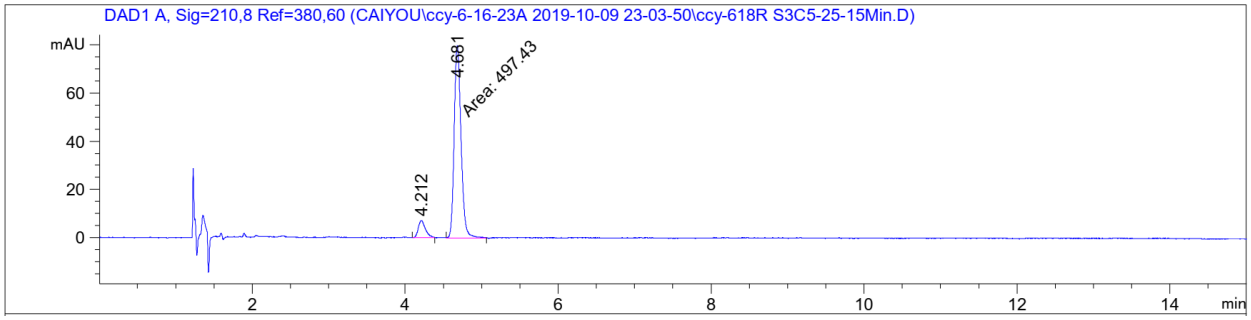


Figure 2, entry 19, (*S,S*)-**N1***: 93:7 dr; (*R,R*)-**N1***: 8:92 dr.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.162	MM	0.1087	682.21045	104.61682	93.4417
2	4.646	MM	0.0996	47.88159	8.01275	6.5583



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.212	BB	0.0954	45.84604	7.00511	8.4388
2	4.681	MM	0.1040	497.42990	79.70731	91.5612

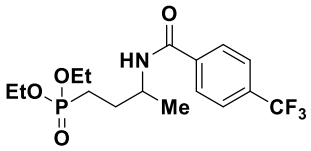
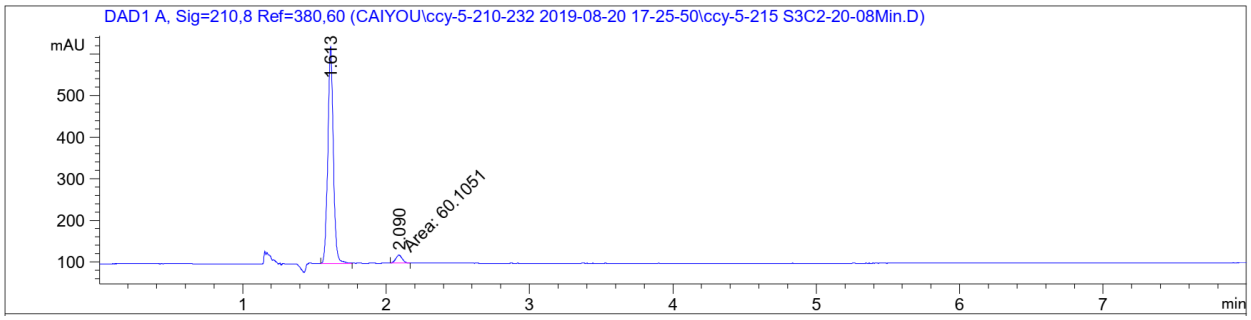
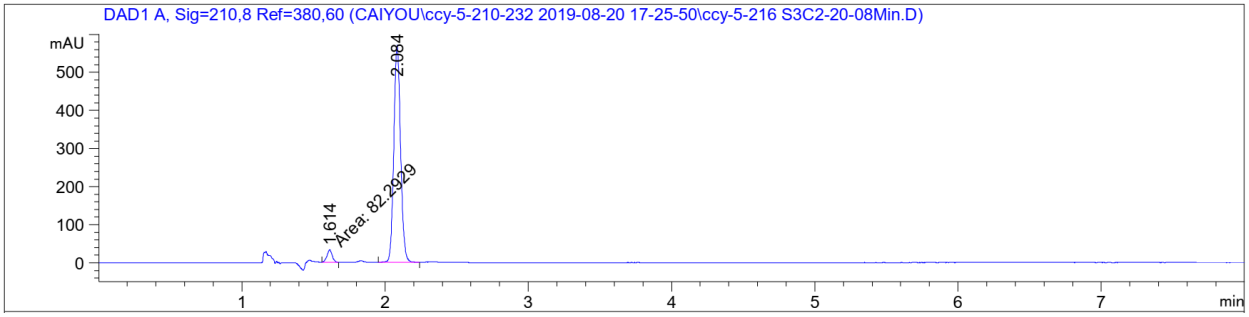


Figure 3, entry 20, (*S,S*)-**N1***: 92% ee; (*R,R*)-**N1***: 92% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.613	BB	0.0400	1384.51526	520.54181	95.8394
2	2.090	MM	0.0526	60.10507	19.05381	4.1606



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.614	MM	0.0420	82.29295	32.63407	4.1906
2	2.084	VB	0.0505	1881.45862	570.62915	95.8094

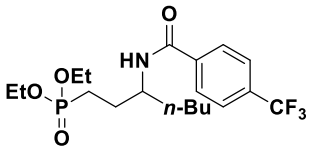
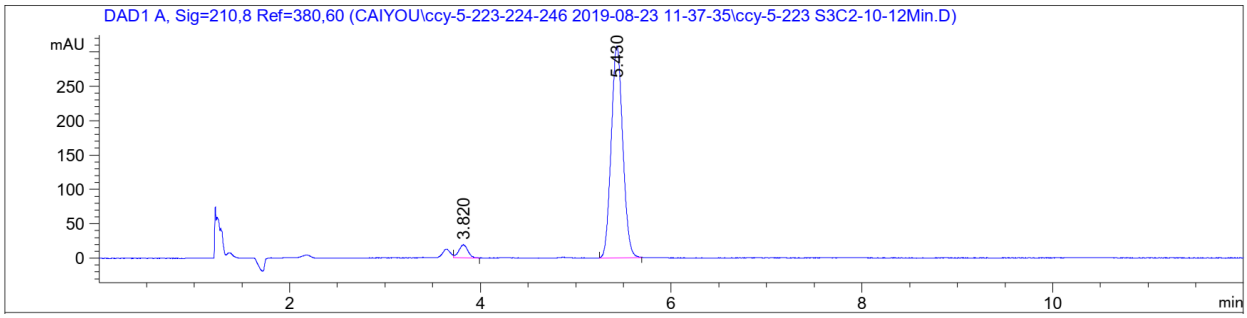
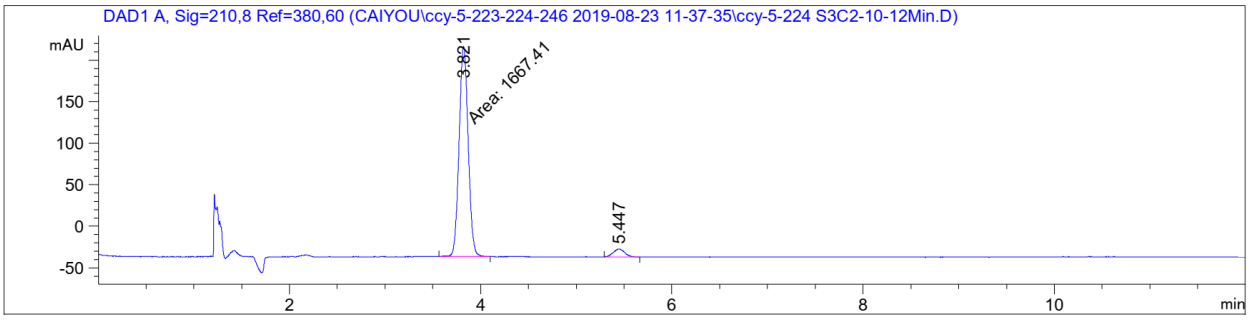


Figure 3, entry 21, (*S,S*)-**N1***: 91% ee; (*R,R*)-**N1***: 91% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.820	VB	0.0952	125.14185	18.91561	4.6029
2	5.430	BB	0.1303	2593.60156	307.81802	95.3971



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.821	MM	0.1099	1667.40955	252.75470	95.4474
2	5.447	BB	0.1211	79.53188	9.55869	4.5526

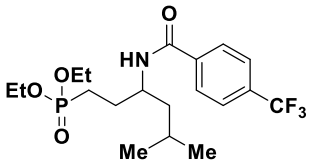
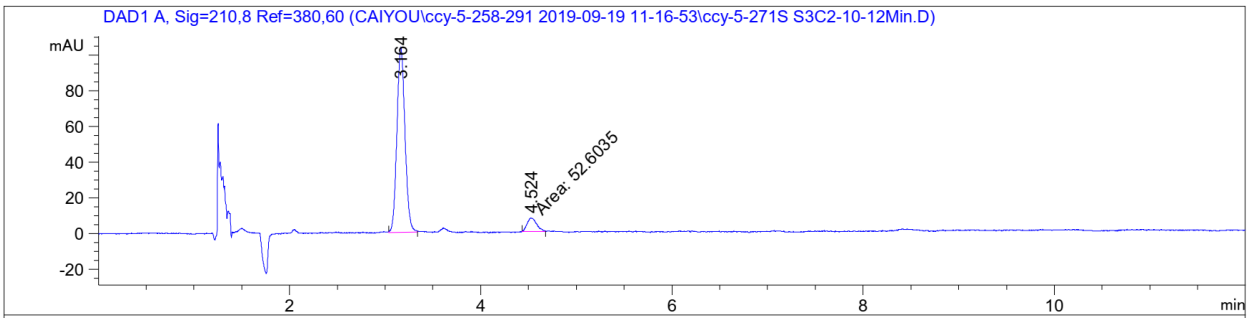
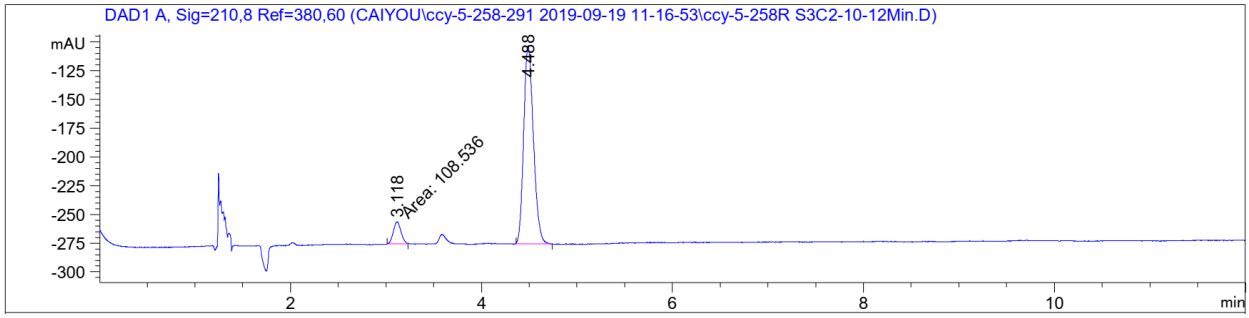


Figure 3, entry 22, (*S,S*)-**N1***: 84% ee; (*R,R*)-**N1***: 84% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.164	BB	0.0902	604.73956	103.45106	91.9976
2	4.524	MM	0.1162	52.60350	7.54778	8.0024



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.118	MM	0.0947	108.53644	19.09406	8.1628
2	4.488	BB	0.1096	1221.11060	172.49597	91.8372

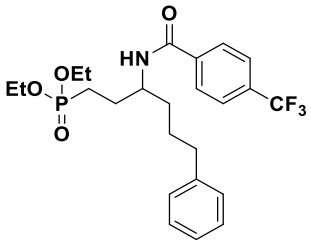
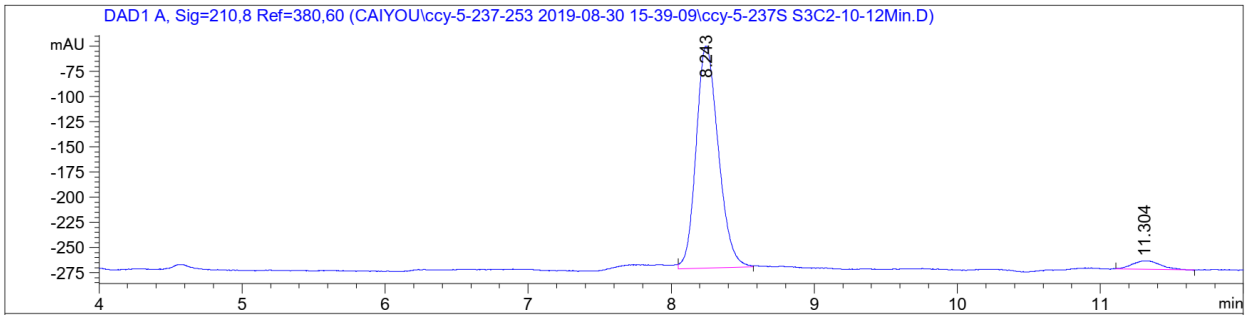
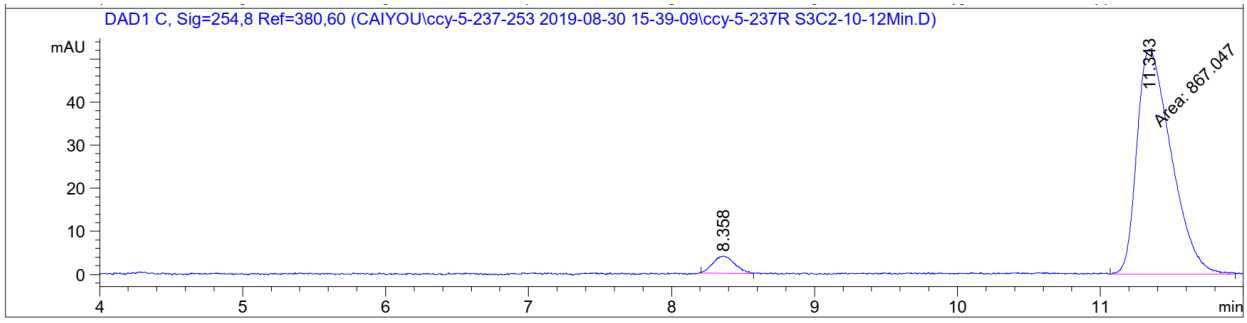


Figure 3, entry 23, (*S,S*)-**N1***: 91% ee; (*R,R*)-**N1***: 91% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.243	BB	0.1672	2384.75073	220.47893	95.5775
2	11.304	BB	0.1693	110.34647	8.18479	4.4225



Signal 3: DAD1 C, Sig=254,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.358	BB	0.1268	42.60990	4.01467	4.6842
2	11.343	MM	0.2770	867.04706	52.17092	95.3158

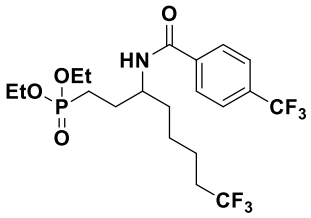
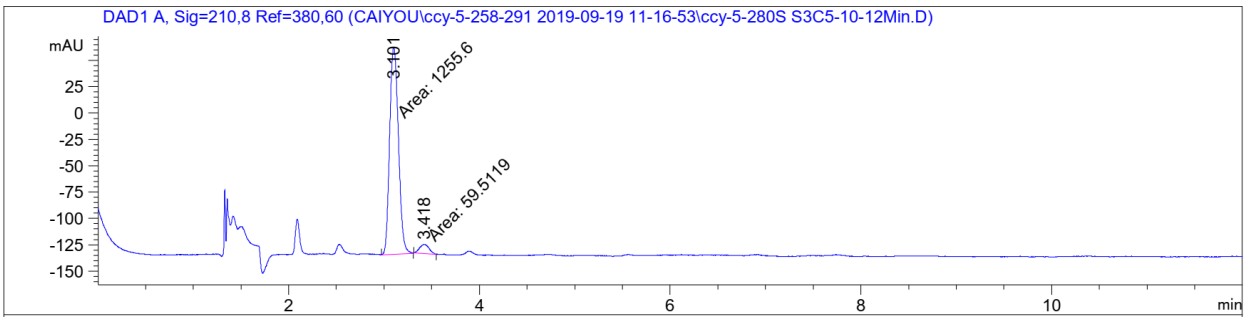
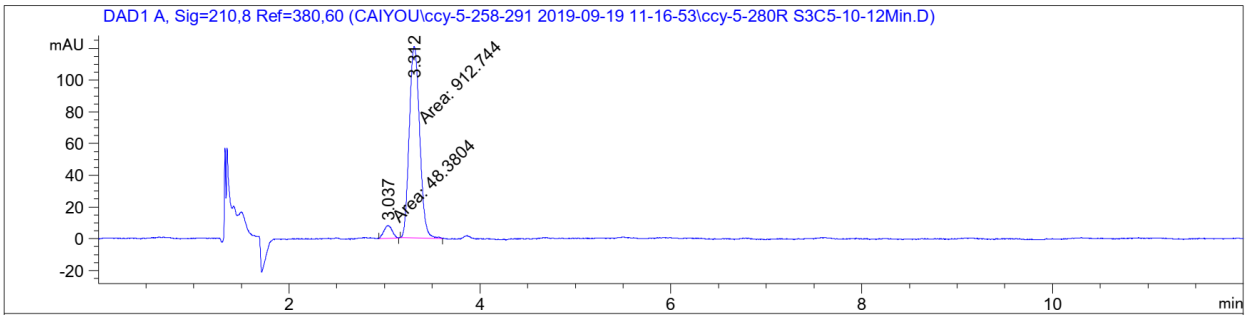


Figure 3, entry 24, (*S,S*)-**N1***: 91% ee; (*R,R*)-**N1***: 90% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.101	MM	0.1065	1255.60388	196.49840	95.4748
2	3.418	MM	0.1155	59.51191	8.58440	4.5252



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.037	MM	0.1019	48.38036	7.91572	5.0337
2	3.312	MM	0.1260	912.74390	120.74677	94.9663

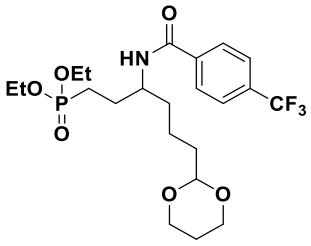
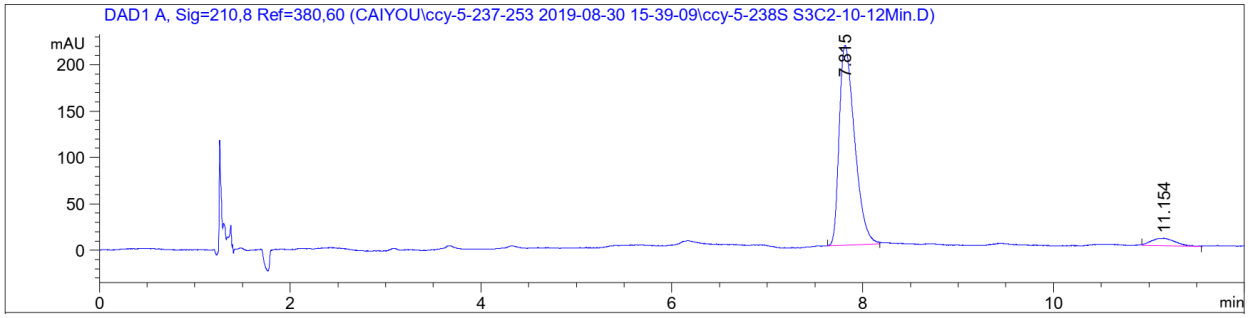
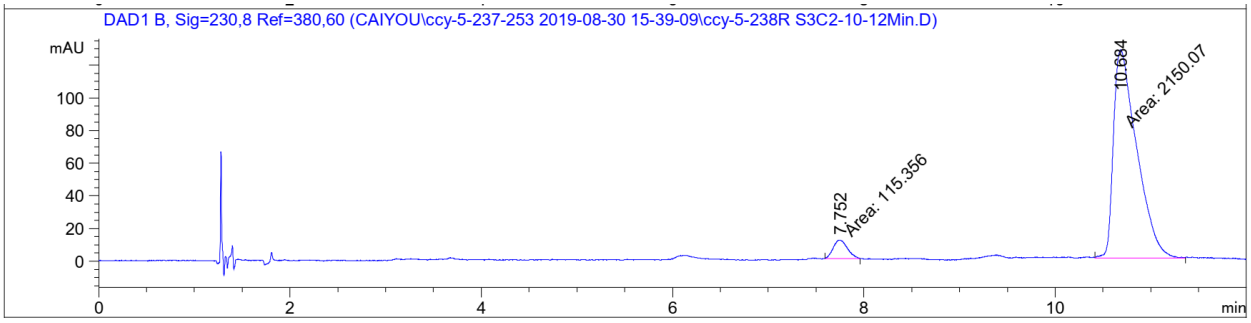


Figure 3, entry 25, (*S,S*)-**N1***: 91% ee; (*R,R*)-**N1***: 91% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.815	BB	0.1692	875.61658	79.07231	95.2293
2	11.156	MM	0.2548	43.86587	2.86937	4.7707



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.753	MM	0.1724	115.14120	11.13390	4.5644
2	10.683	MM	0.2998	2407.45190	133.85228	95.4356

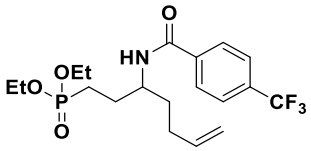
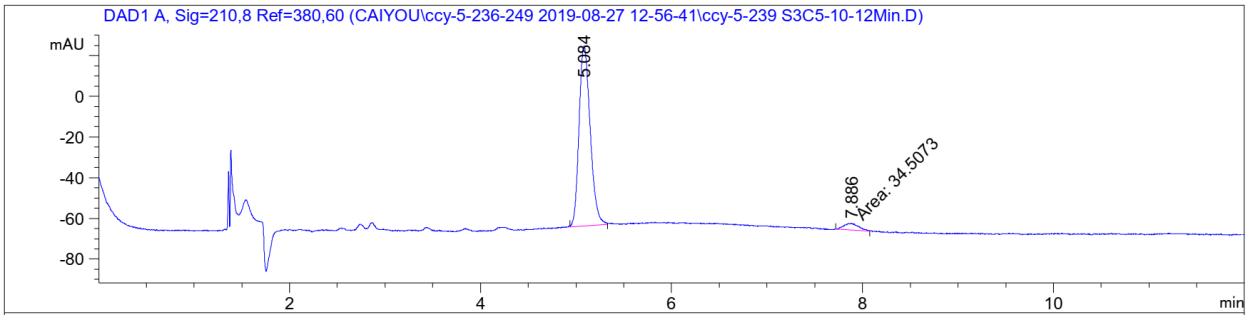
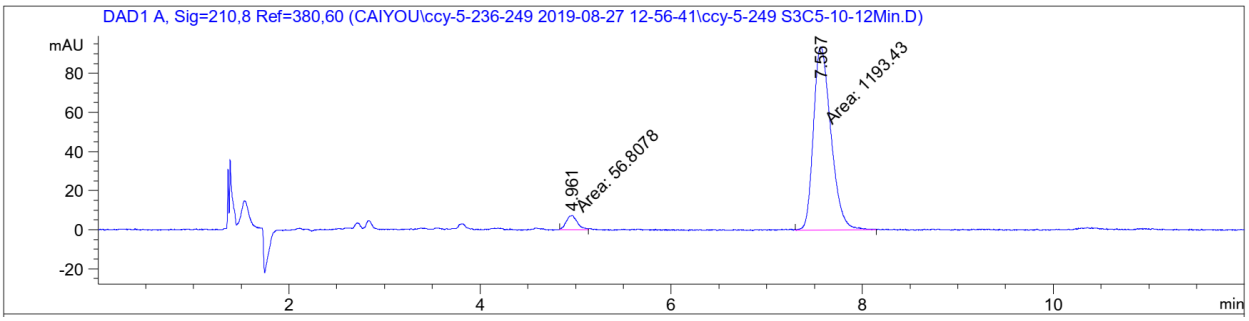


Figure 3, entry 26, (*S*,*S*)-**N1***: 91% ee; (*R*,*R*)-**N1***: 91% ee



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.084	BB	0.1247	718.01251	88.44283	95.4144
2	7.886	MM	0.1768	34.50727	3.25320	4.5856



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.961	MM	0.1341	56.80785	7.06135	4.5438
2	7.567	MM	0.2123	1193.43213	93.66908	95.4562

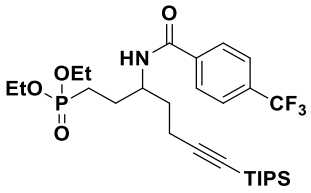
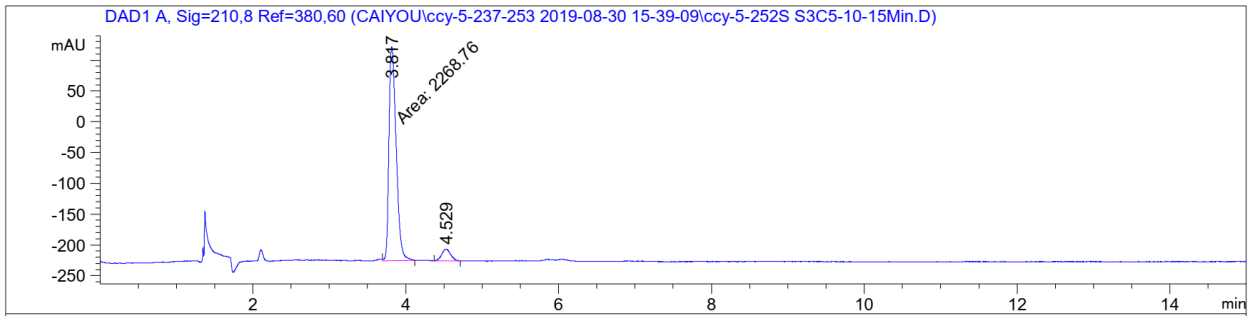
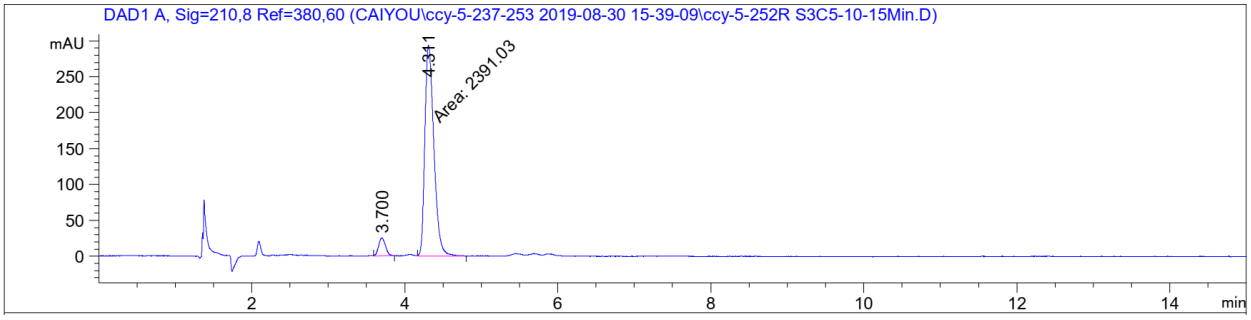


Figure 3, entry 27, (*S,S*)-**N1***: 88% ee; (*R,R*)-**N1***: 88% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.817	FM	0.1089	2268.75781	347.27454	93.7009
2	4.529	BV	0.1102	152.51761	18.89904	6.2991



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.700	BB	0.0948	155.18256	24.87613	6.0946
2	4.311	MM	0.1359	2391.02881	293.31183	93.9054

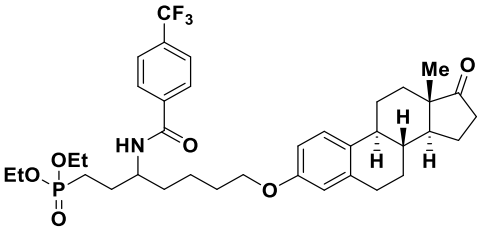
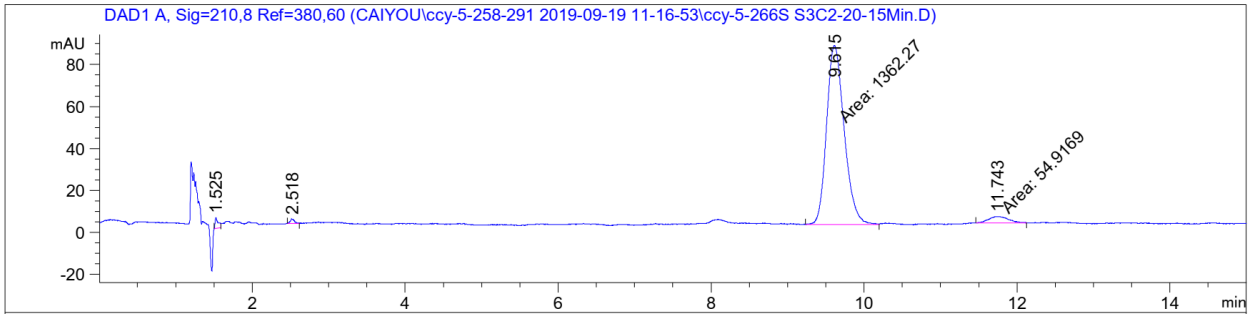
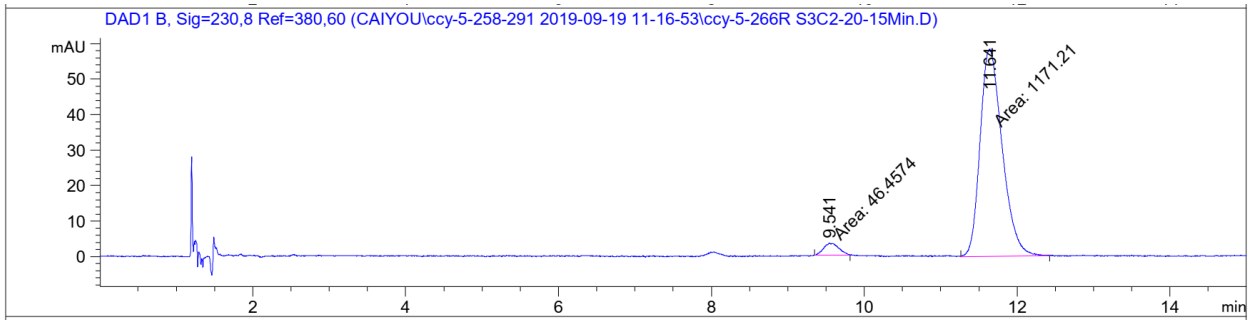


Figure 3, entry 28, (*S*,*S*)-**N1***: 96:4 dr; (*R*,*R*)-**N1***: 4:96 dr.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.616	MM	0.2656	878.37946	55.12916	95.8094
2	11.770	MM	0.2995	38.41973	2.13792	4.1906



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.541	MM	0.2312	46.45742	3.34957	3.8153
2	11.641	MM	0.3344	1171.20764	58.37975	96.1847

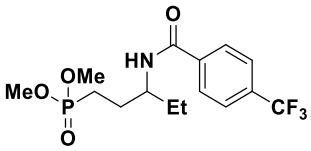
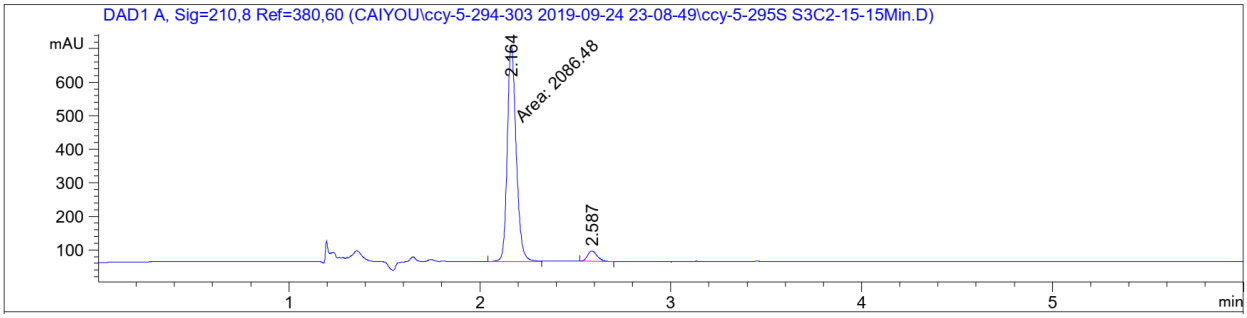
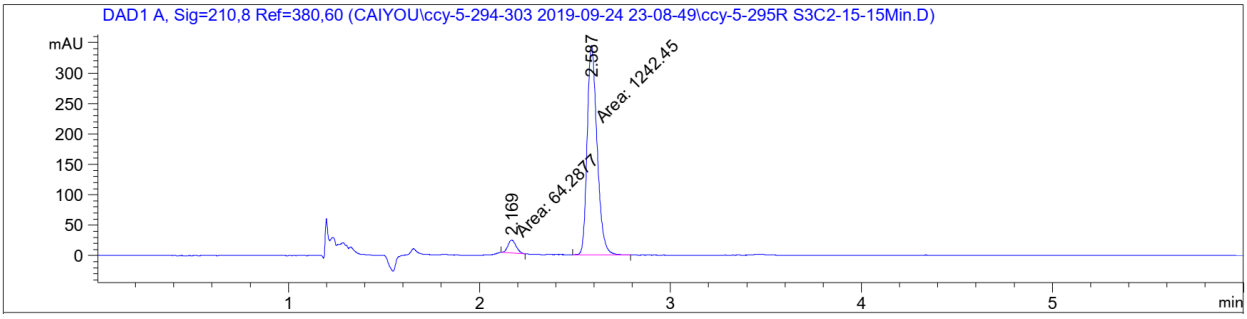


Figure 3, entry 29, (*S*,*S*)-**N1***: 90% ee; (*R*,*R*)-**N1***: 90% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.164	MM	0.0539	2086.48413	645.70648	94.9280
2	2.587	BB	0.0545	111.48103	31.30613	5.0720



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.169	MM	0.0500	64.28765	21.41247	4.9197
2	2.587	MM	0.0602	1242.44946	344.10385	95.0803

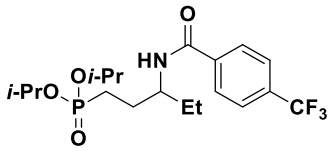
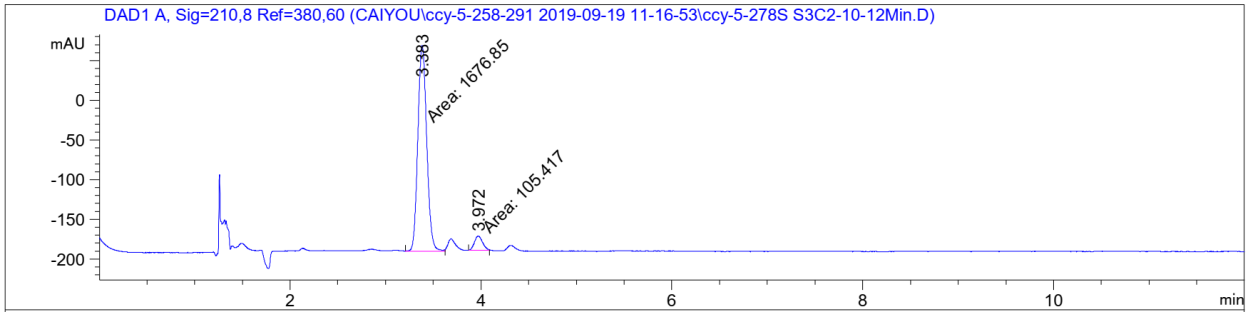
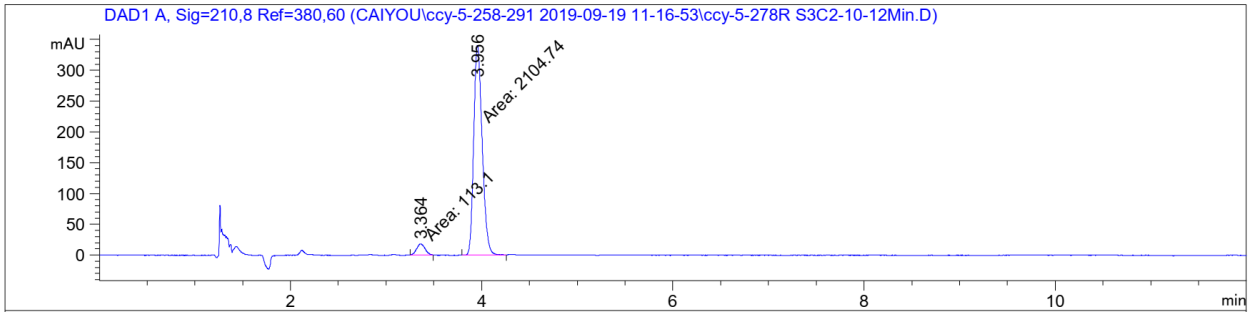


Figure 3, entry 30, (*S*,*S*)-**N1***: 88% ee; (*R*,*R*)-**N1***: 90% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.383	MM	0.1078	1676.85071	259.34061	94.0853
2	3.972	MM	0.0994	105.41650	17.68433	5.9147



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.364	MM	0.1026	113.10017	18.37359	5.0996
2	3.956	MM	0.1030	2104.73804	340.66235	94.9004

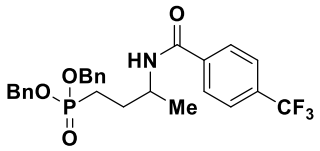
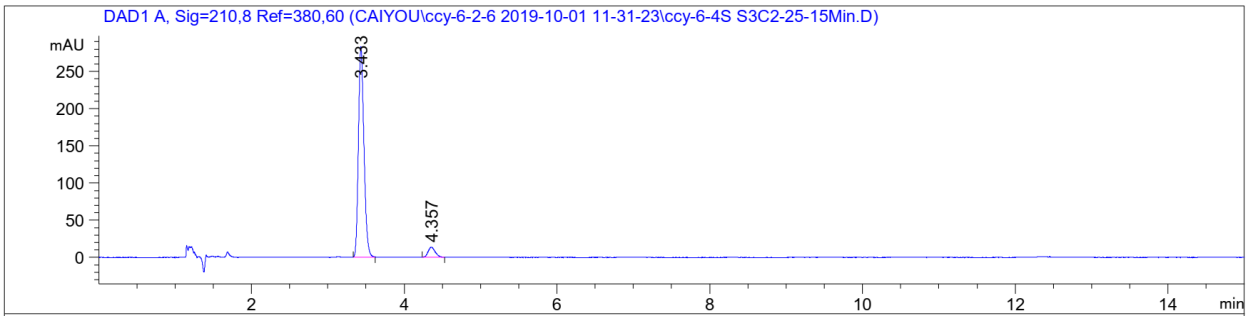
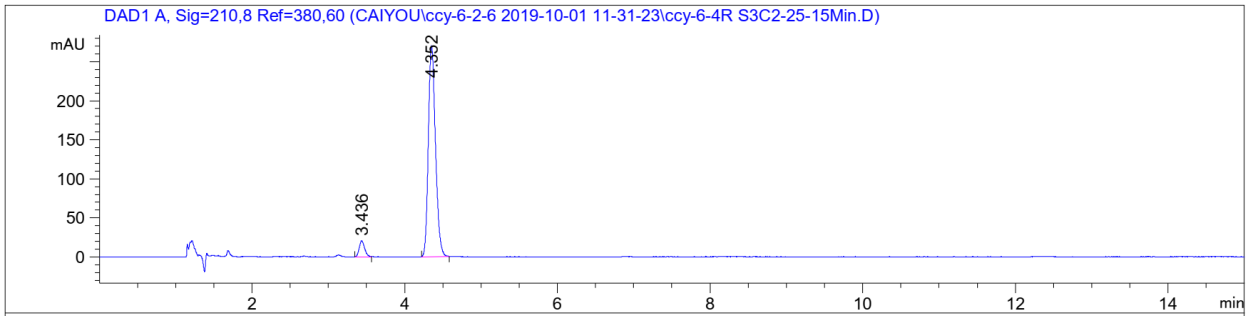


Figure 3, entry 31, (*S,S*)-**N1***: 89% ee; (*R,R*)-**N1***: 89% ee.



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.433	BB	0.0765	591.77655	117.94294	94.3797
2	4.357	BB	0.0912	35.23991	5.54301	5.6203



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.436	BB	0.0754	102.56445	20.48952	5.5394
2	4.352	BB	0.0997	1748.97559	269.71906	94.4606

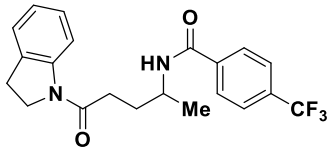
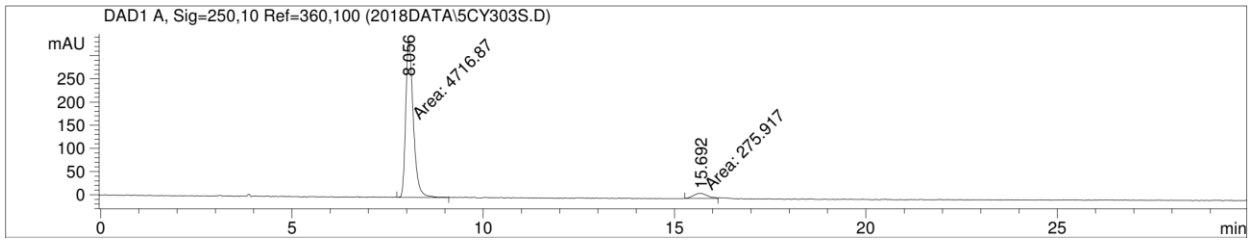
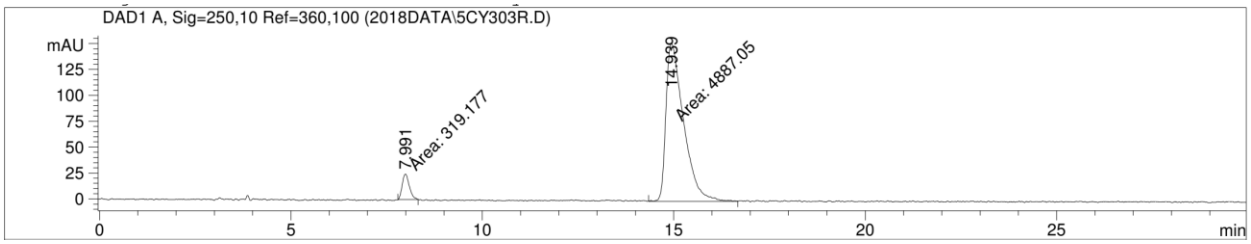


Figure 3, entry 32, (*S,S*)-**N2***: 89% ee; (*R,R*)-**N2***: 88% ee.



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.056	MM	0.2340	4716.86719	336.01587	94.4737
2	15.692	MM	0.4271	275.91714	10.76654	5.5263



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.991	MM	0.2169	319.17709	24.52381	6.1307
2	14.939	MM	0.5352	4887.04883	152.18561	93.8693

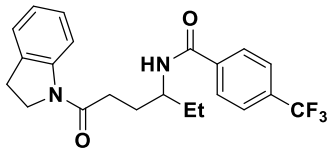
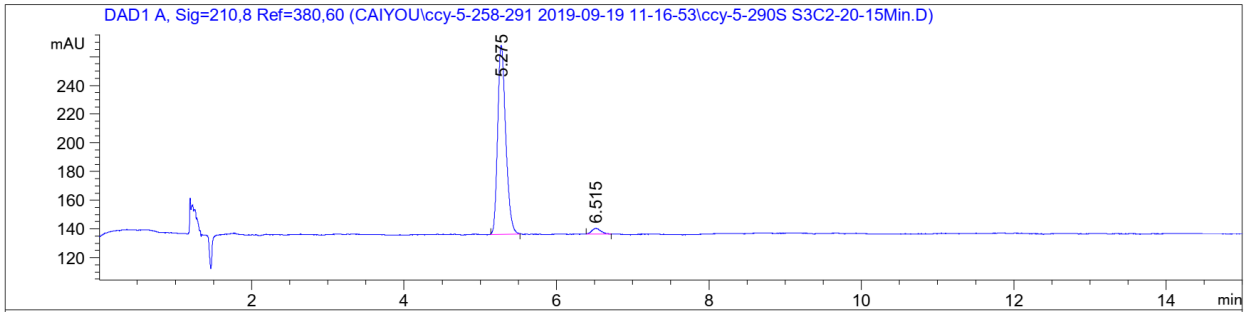
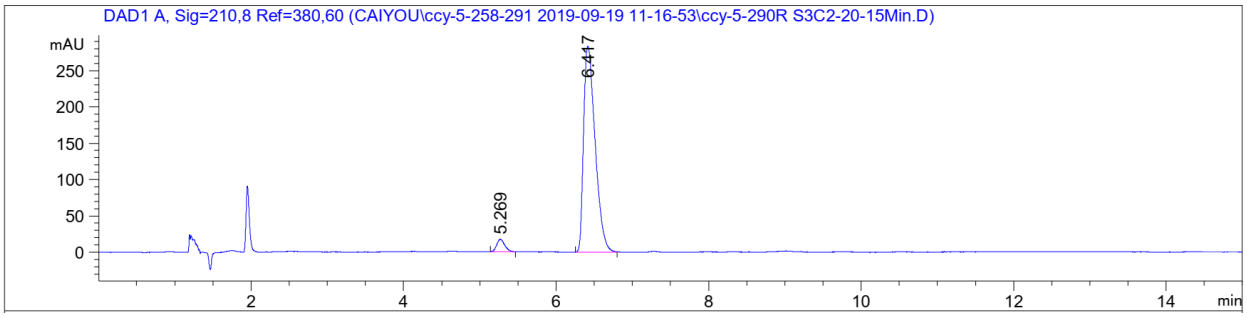


Figure 3, entry 33, (*S,S*)-**N2***: 93% ee; (*R,R*)-**N2***: 92% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.275	BB	0.1123	974.09924	131.70381	96.6285
2	6.515	BB	0.1229	33.98723	3.93139	3.3715



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.269	BB	0.1084	125.99419	17.21551	4.0648
2	6.417	BB	0.1623	2973.63647	283.56744	95.9352

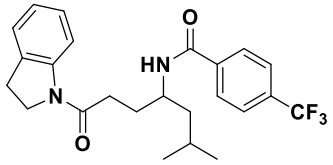
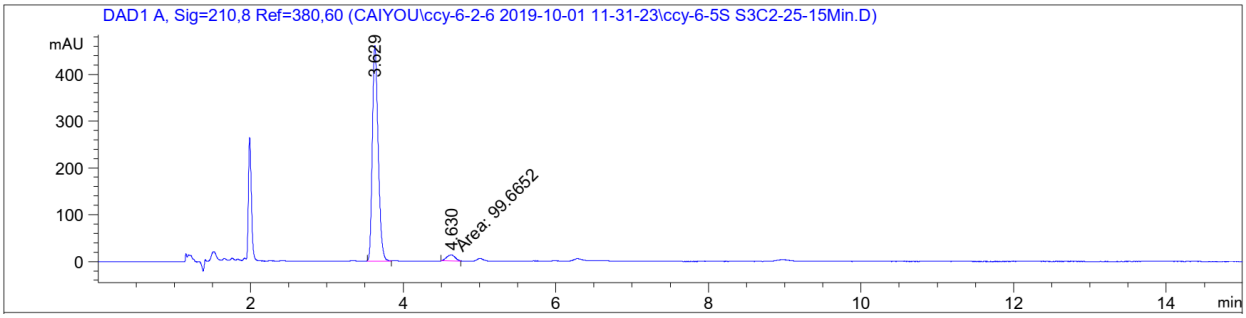
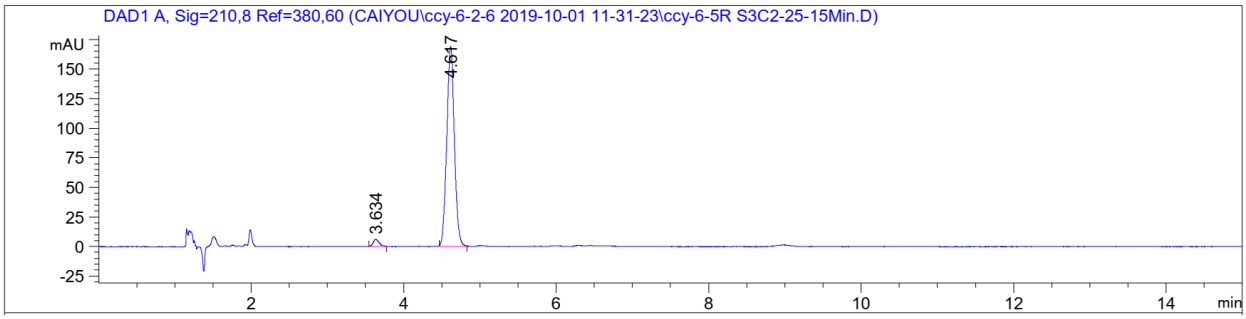


Figure 3, entry 34, (*S,S*)-**N2***: 93% ee; (*R,R*)-**N2***: 94% ee.



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.629	BB	0.0815	1408.34326	267.18625	96.5844
2	4.616	BB	0.1308	49.80463	6.06563	3.4156



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.634	BB	0.0820	33.43981	6.09367	2.7768
2	4.617	BB	0.1068	1170.83118	168.97304	97.2232

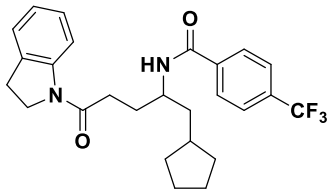
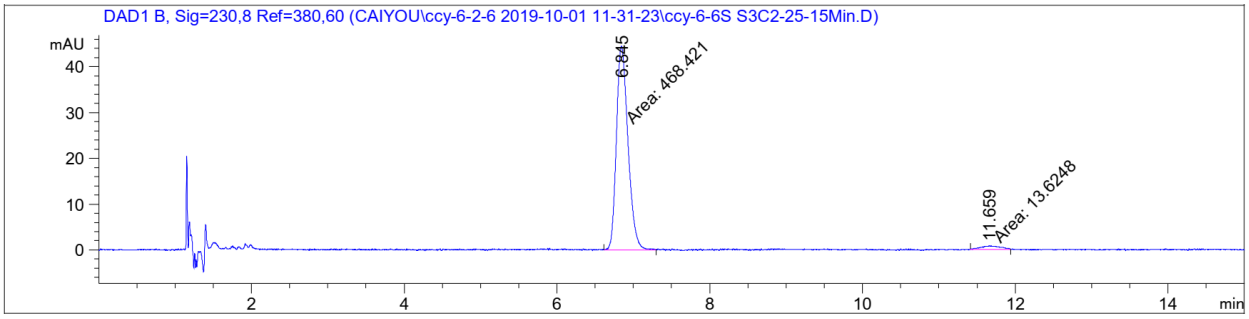
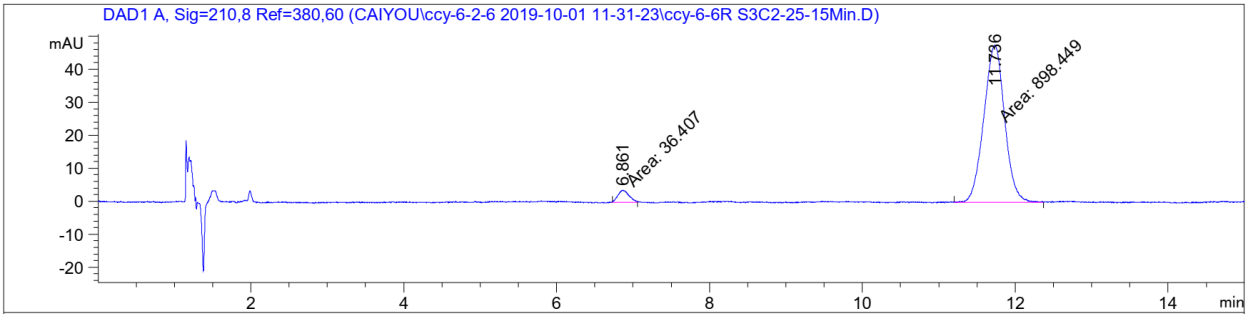


Figure 3, entry 35, (*S*,*S*)-**N2***: 94% ee; (*R*,*R*)-**N2***: 93% ee



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.845	MM	0.1754	468.42142	44.49961	97.1735
2	11.659	MM	0.2914	13.62483	7.79159e-1	2.8265



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.853	MM	0.1609	19.13278	1.98190	3.5923
2	11.737	MM	0.3138	513.46930	27.26752	96.4077

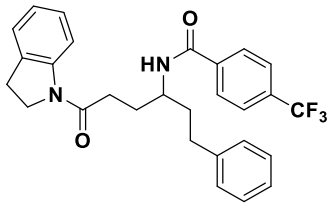
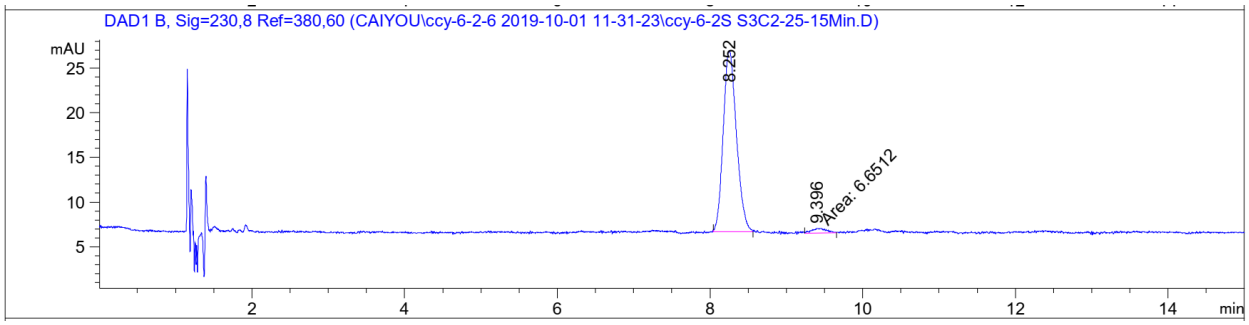
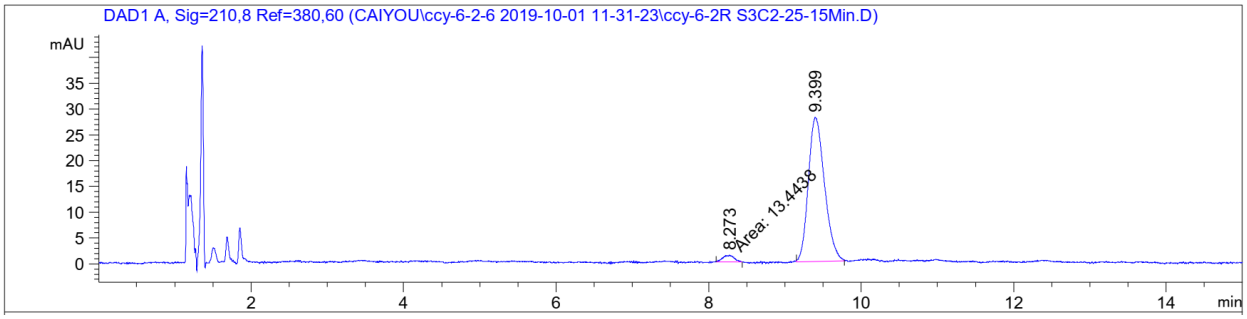


Figure 3, entry 36, (*S,S*)-**N2***: 95% ee; (*R,R*)-**N2***: 94% ee.



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.252	BB	0.1697	244.48857	20.27495	97.3516
2	9.396	MM	0.2175	6.65120	5.09702e-1	2.6484



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.273	MM	0.1705	13.44377	1.31433	3.1677
2	9.399	BB	0.2119	410.96039	27.88572	96.8323

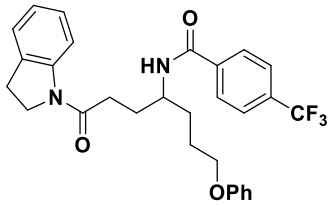
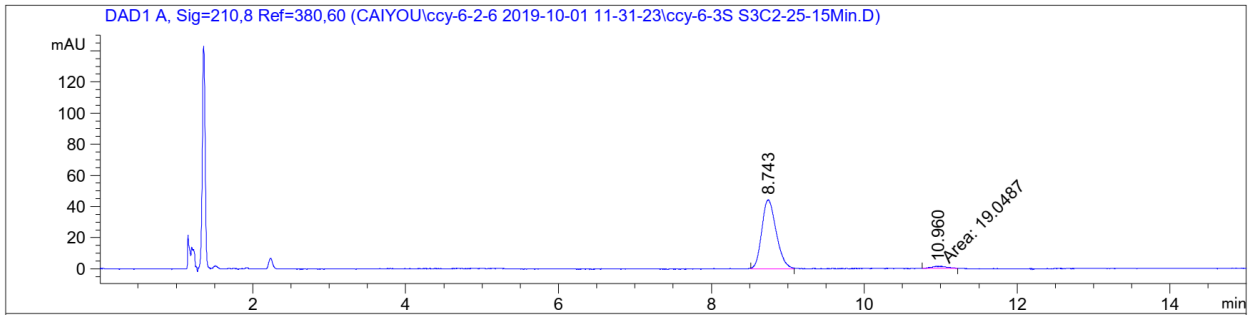
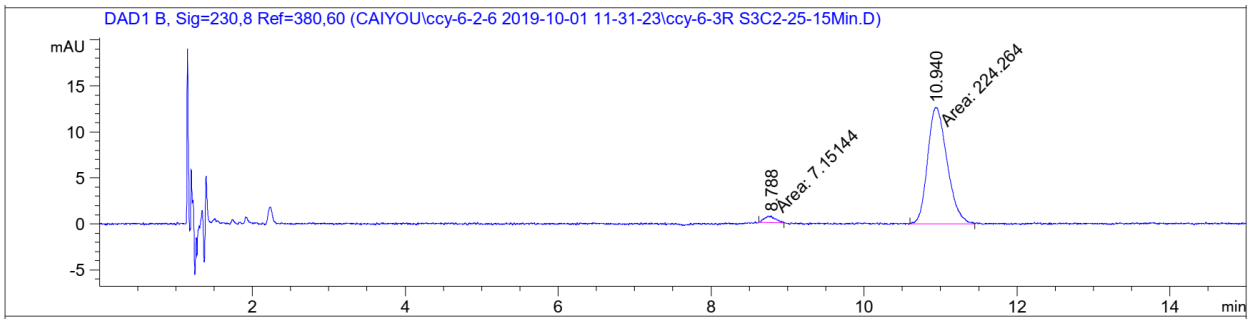


Figure 3, entry 37, (*S,S*)-**N2***: 94% ee; (*R,R*)-**N2***: 94% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.743	BB	0.1877	578.75342	44.22142	96.8135
2	10.960	MM	0.2481	19.04875	1.27972	3.1865



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.788	MM	0.1678	7.15144	7.10455e-1	3.0903
2	10.940	MM	0.2949	224.26398	12.67449	96.9097

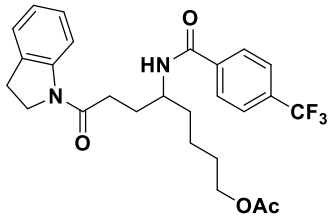
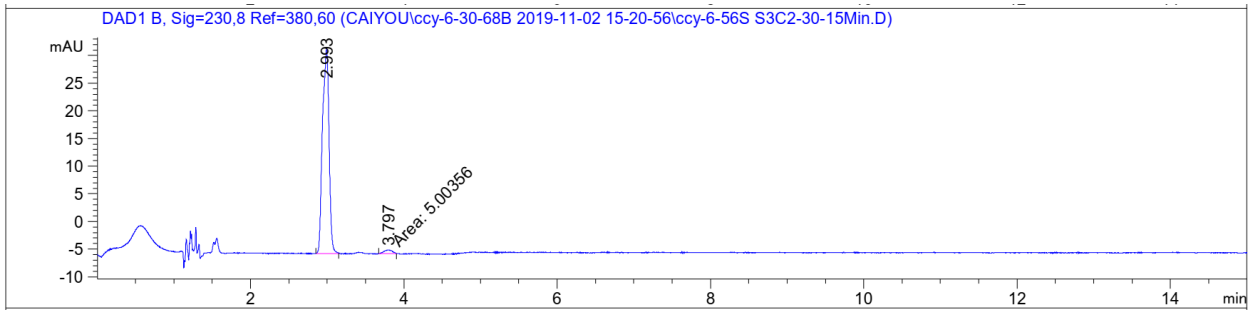
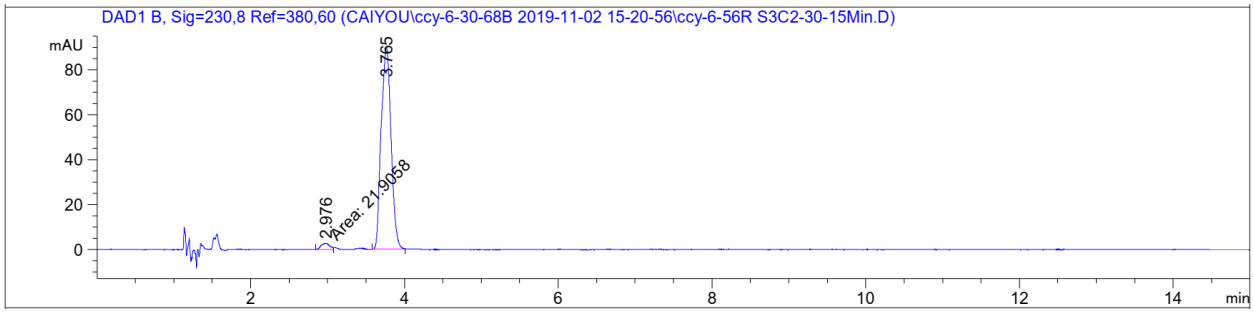


Figure 3, entry 38, (*S,S*)-**N2***: 95% ee; (*R,R*)-**N2***: 95% ee.



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.993	BB	0.0832	220.27792	37.11680	97.7790
2	3.797	MM	0.1292	5.00356	6.45578e-1	2.2210



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.976	MF	0.1306	21.90578	2.79456	2.6547
2	3.765	BB	0.1301	803.25458	89.99300	97.3453

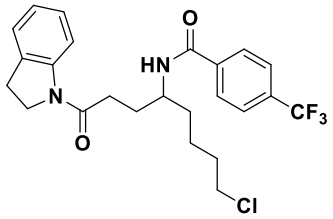
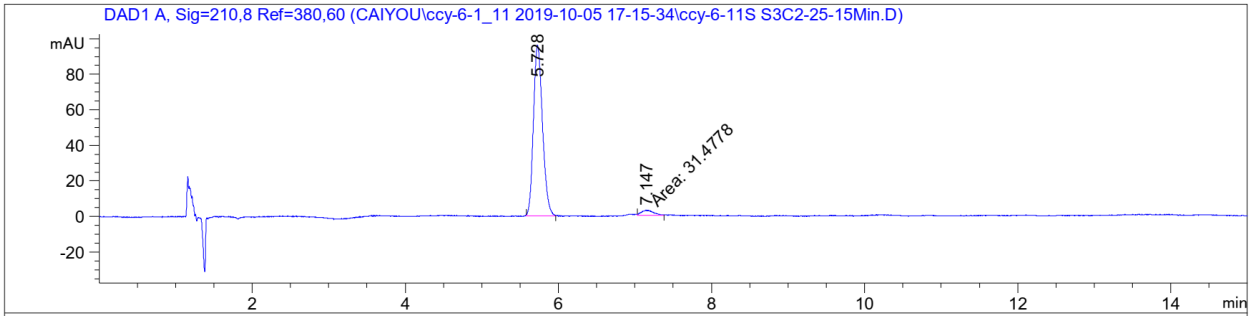
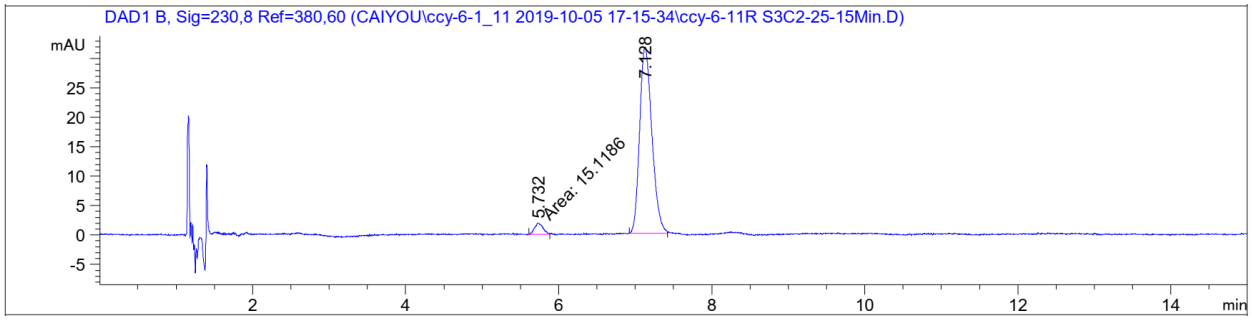


Figure 3, entry 39, (*S,S*)-**N2***: 92% ee; (*R,R*)-**N2***: 92% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.728	BB	0.1263	793.32452	96.11656	96.1836
2	7.147	MM	0.1810	31.47780	2.89862	3.8164



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.735	BB	0.1014	24.82868	3.13528	3.9386
2	7.128	BB	0.1667	605.55981	54.45048	96.0614

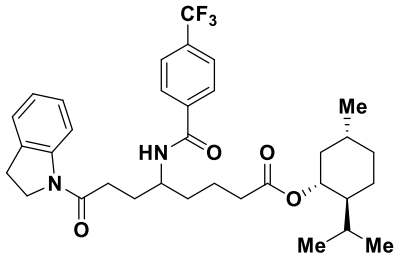
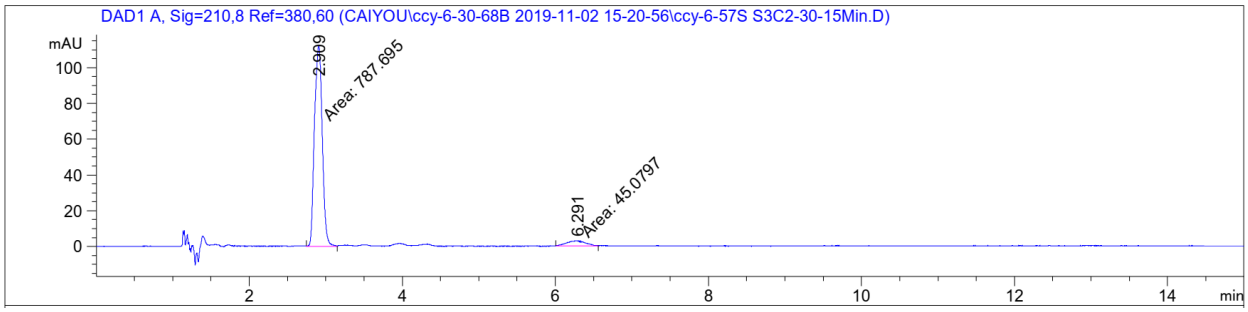
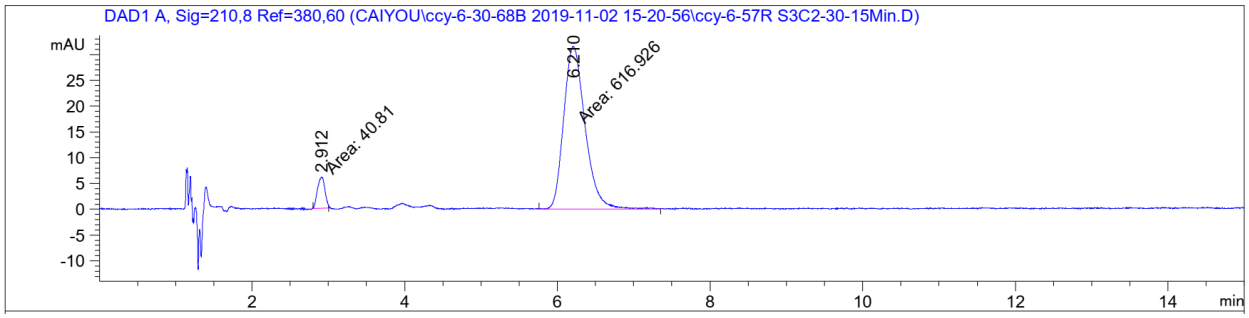


Figure 3, entry 40, (*S,S*)-**N2***: 95:5 dr; (*R,R*)-**N2***: 6:94 dr.



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.909	BB	0.1143	443.66629	63.69032	94.8727
2	6.291	MM	0.2410	23.97728	1.65817	5.1273



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.913	MM	0.1131	8.16554	1.20350	6.0696
2	6.210	MM	0.3293	126.36655	6.39609	93.9304

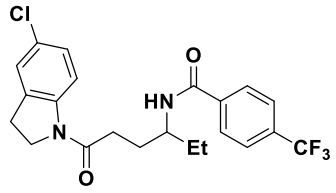
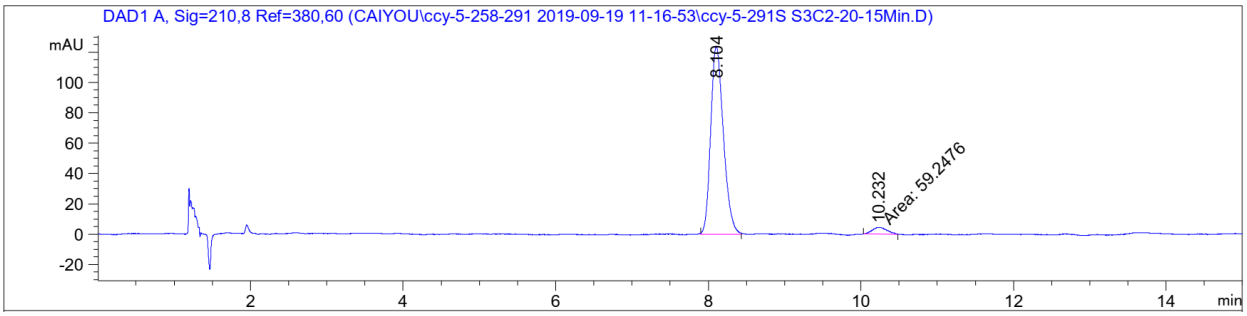
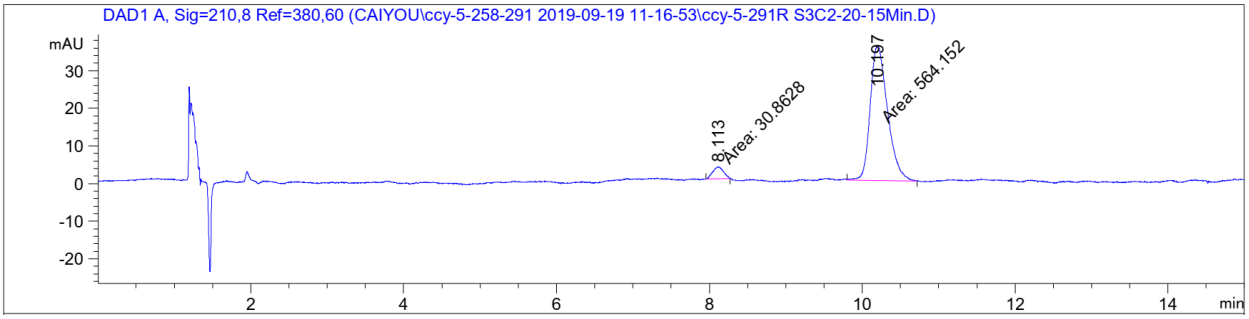


Figure 3, entry 41, (*S,S*)- **L2**: 92% ee; (*R,R*)- **L2**: 90% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.104	BB	0.1767	1428.49548	123.74732	96.0176
2	10.232	MM	0.2238	59.24757	4.41172	3.9824



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.113	MM	0.1633	30.86276	3.14955	5.1869
2	10.197	MM	0.2624	564.15234	35.82718	94.8131

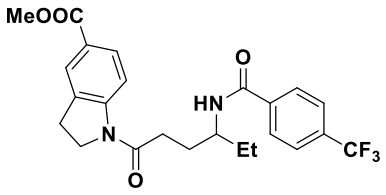
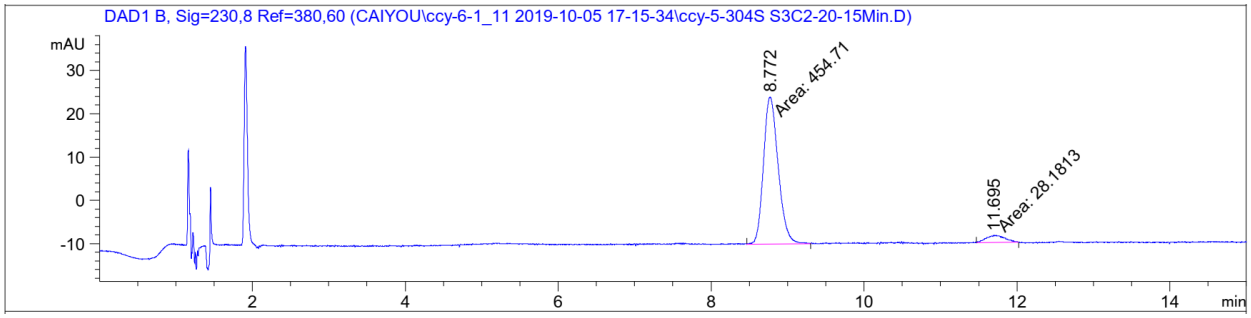
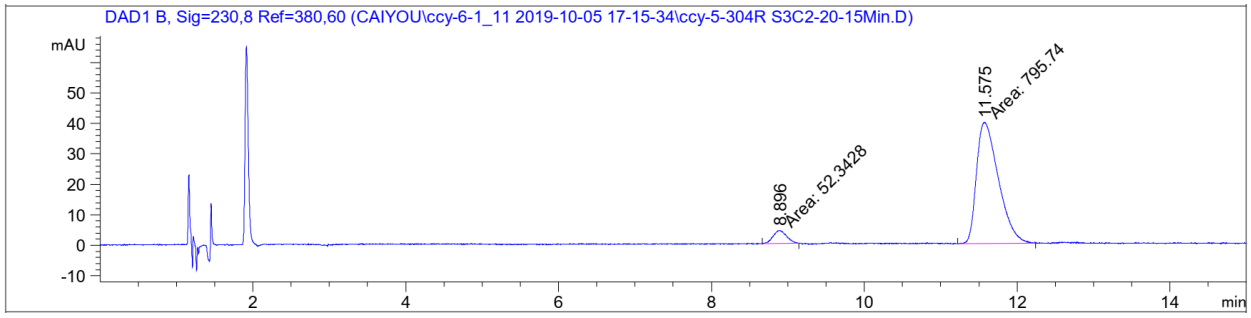


Figure 3, entry 42, (*S,S*)- **L2**: 88% ee; (*R,R*)- **L2**: 88% ee.



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.772	MM	0.2229	454.70975	34.00561	94.1641
2	11.695	MM	0.2787	28.18125	1.68530	5.8359



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.896	MM	0.2058	52.34280	4.23831	6.1719
2	11.575	MM	0.3337	795.74017	39.74763	93.8281

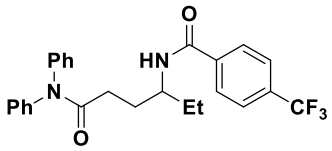
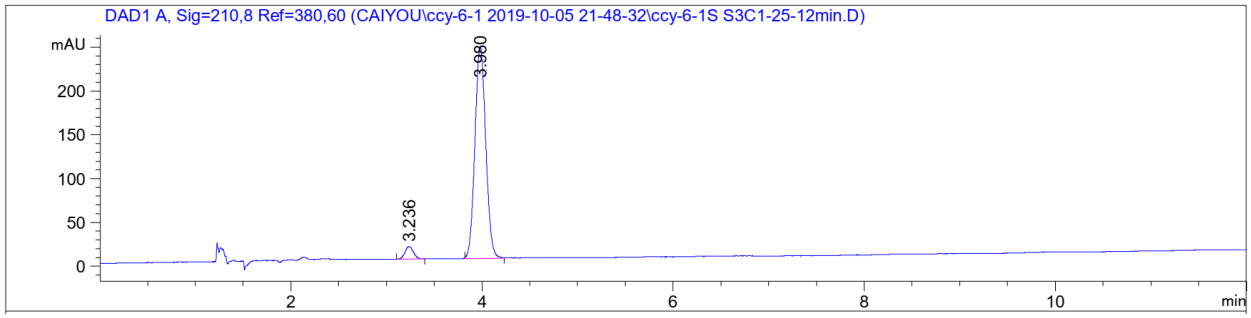
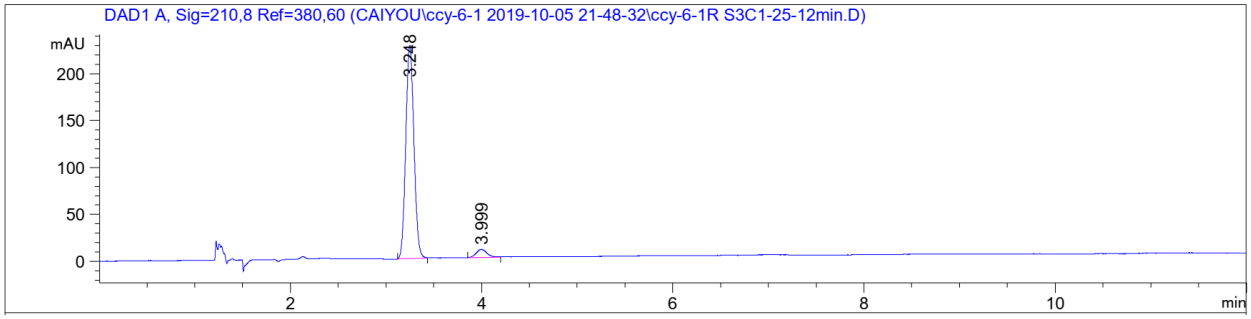


Figure 3, entry 43, (*S,S*)-**N2***: 91% ee; (*R,R*)-**N2***: 91% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.236	BB	0.0955	87.46198	14.26827	4.3929
2	3.980	BB	0.1227	1903.52893	242.15428	95.6071



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.248	BB	0.0923	1349.13940	226.97331	95.3760
2	3.999	BB	0.1193	65.40865	8.44790	4.6240

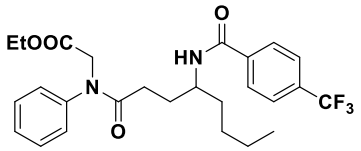
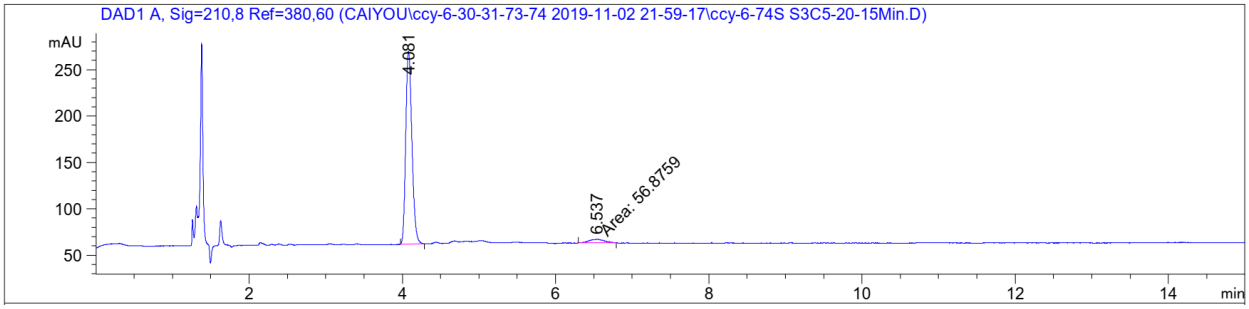
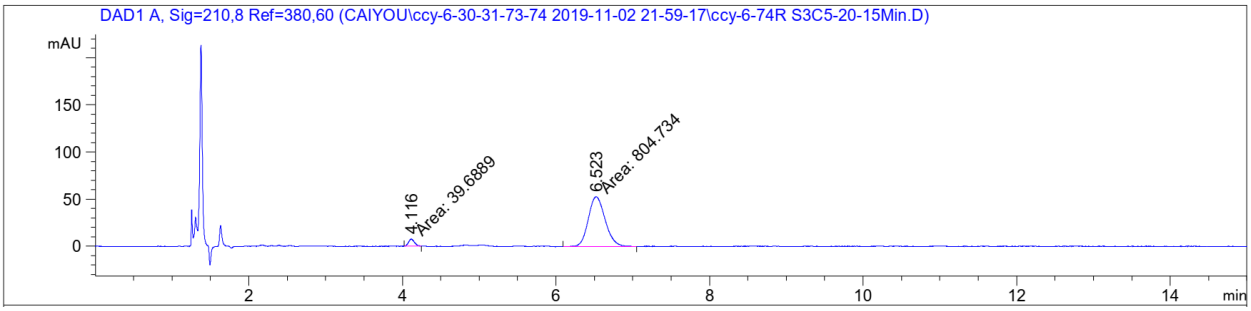


Figure 3, entry 44, (*S,S*)-**N2***: 91% ee; (*R,R*)-**N2***: 91% ee



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.081	MM	0.0932	836.13232	149.59277	95.6513
2	6.537	MM	0.2339	38.01418	2.70868	4.3487



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.116	MM	0.0876	39.68890	7.55393	4.7001
2	6.523	MM	0.2540	804.73370	52.80102	95.2999

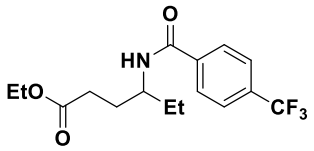
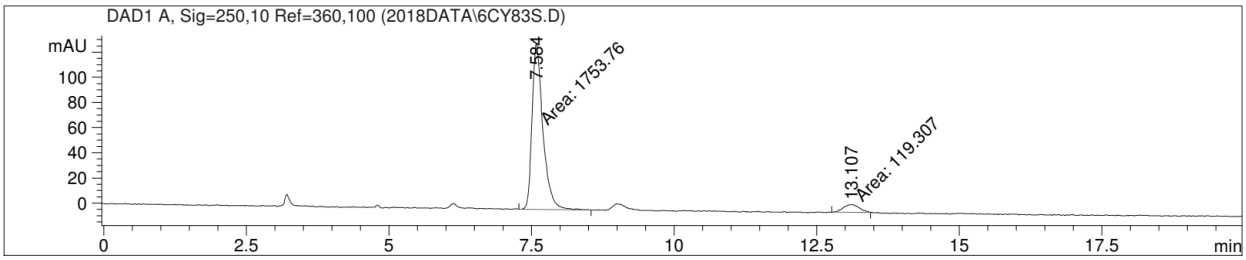
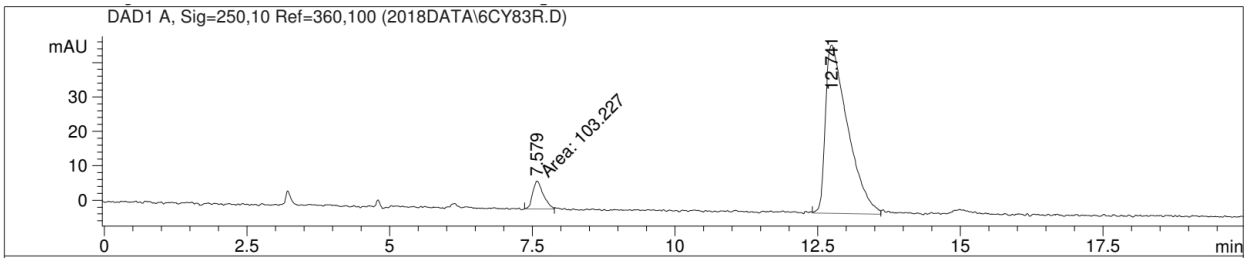


Figure 3, entry 45, (*S,S*)-**N2***: 87% ee; (*R,R*)-**N2***: 87% ee.



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.584	MM	0.2222	1753.76331	131.55490	93.6304
2	13.107	MM	0.3293	119.30732	6.03873	6.3696



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.591	MM	0.2010	19.51369	1.61823	6.5221
2	12.745	MM	0.4565	279.68176	10.21037	93.4779

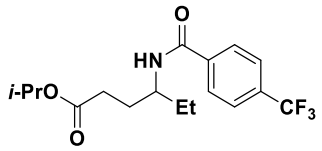
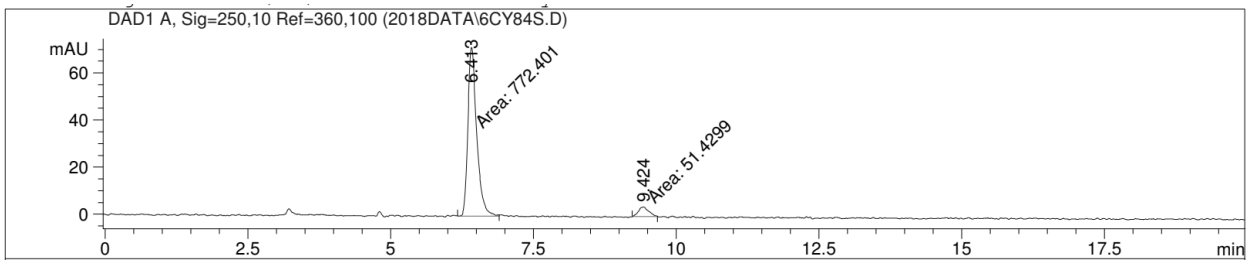
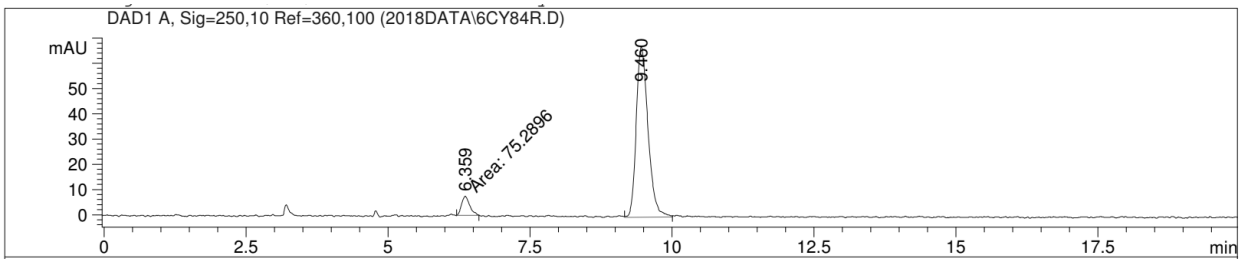


Figure 3, entry 46, (*S,S*)-**N2***: 87% ee; (*R,R*)-**N2***: 87% ee.



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.413	MM	0.1794	772.40143	71.75047	93.7572
2	9.424	MM	0.2109	51.42989	4.06476	6.2428



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.362	MM	0.1548	57.77100	6.22053	6.3863
2	9.461	VB	0.2269	846.84058	57.80430	93.6137

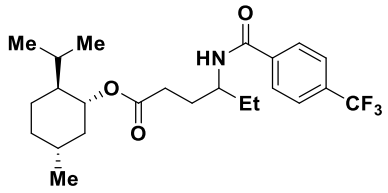
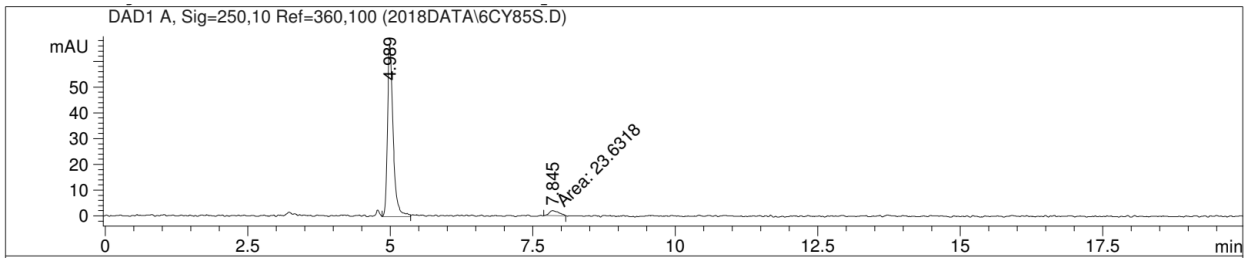
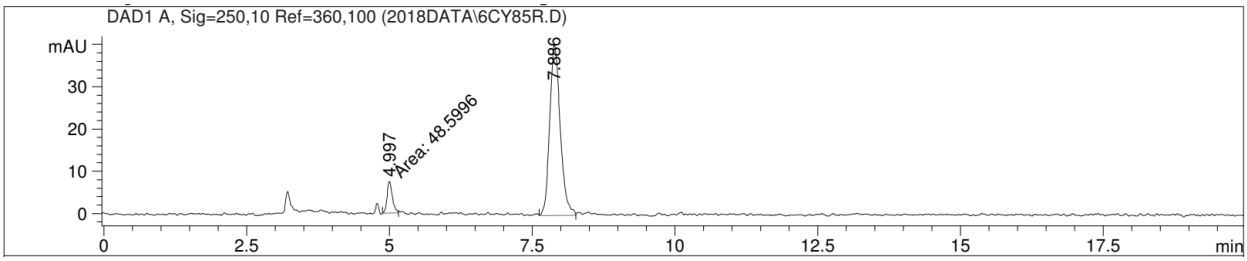


Figure 3, entry 47, (*S,S*)-**N2***: 95:5 dr; (*R,R*)-**N2***: 8:92 dr.



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.989	VB	0.1050	464.30035	66.87356	95.1568
2	7.845	MM	0.1981	23.63175	1.98786	4.8432



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.995	MM	0.1050	101.84682	16.17041	8.1524
2	7.888	VV	0.2006	1147.43347	86.60513	91.8476

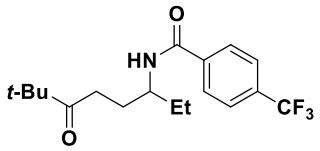
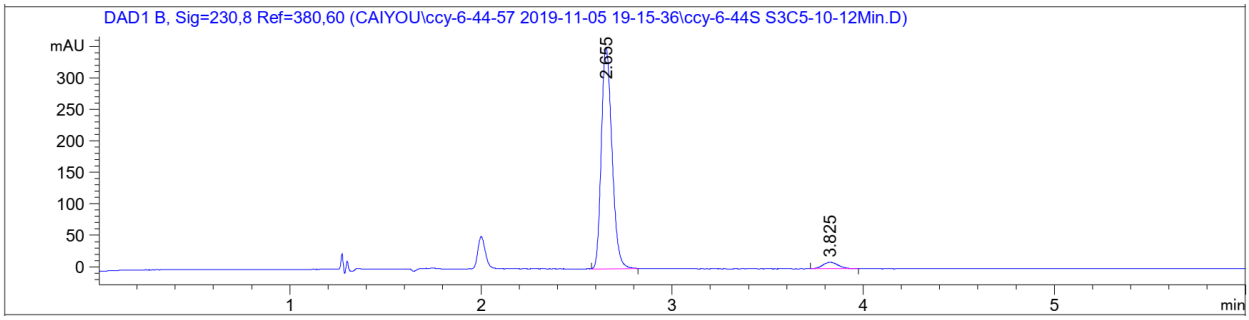
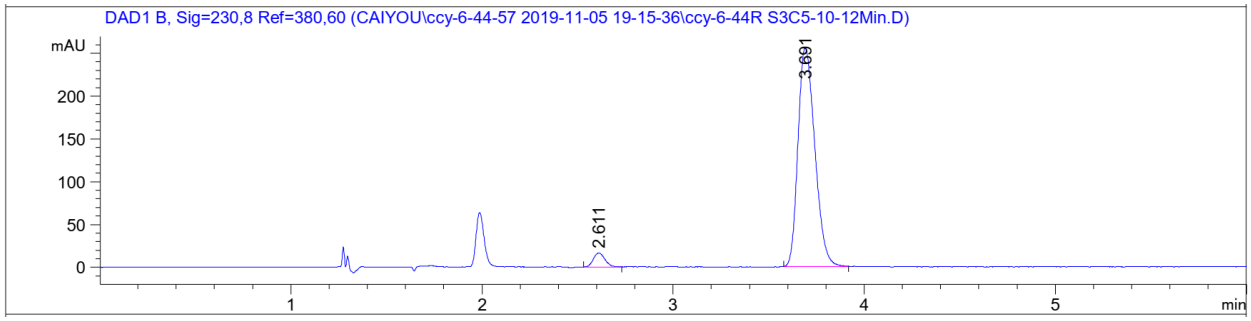


Figure 3, entry 48, (*S,S*)-**N1***: 92% ee; (*R,R*)-**N1***: 92% ee.



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.655	BB	0.0603	1361.80530	351.09692	95.8714
2	3.825	BB	0.0822	58.64429	10.34227	4.1286



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.611	BB	0.0672	68.70337	16.28282	4.1916
2	3.691	BB	0.0966	1570.37097	255.98190	95.8084

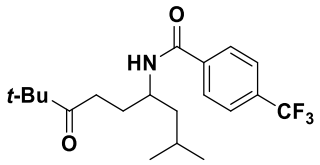
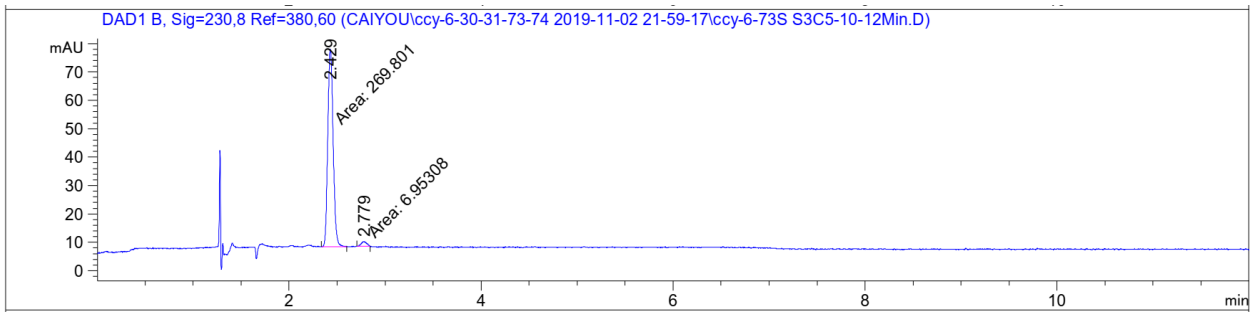
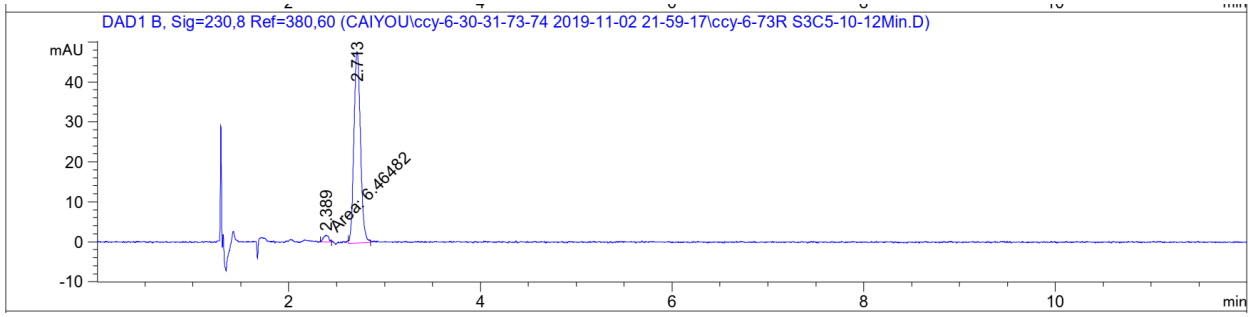


Figure 3, entry 49, (*S,S*)-**N1***: 95% ee; (*R,R*)-**N1***: 95% ee.



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.429	MM	0.0646	269.80096	69.56606	97.4876
2	2.779	MM	0.0655	6.95308	1.76966	2.5124



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.389	MM	0.0649	6.46482	1.66072	2.7480
2	2.713	BB	0.0748	228.79474	47.87027	97.2520

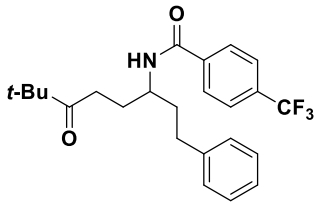
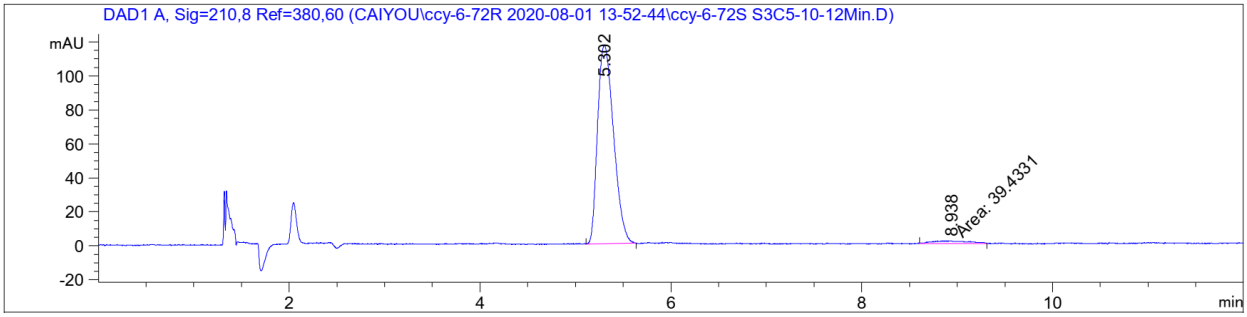
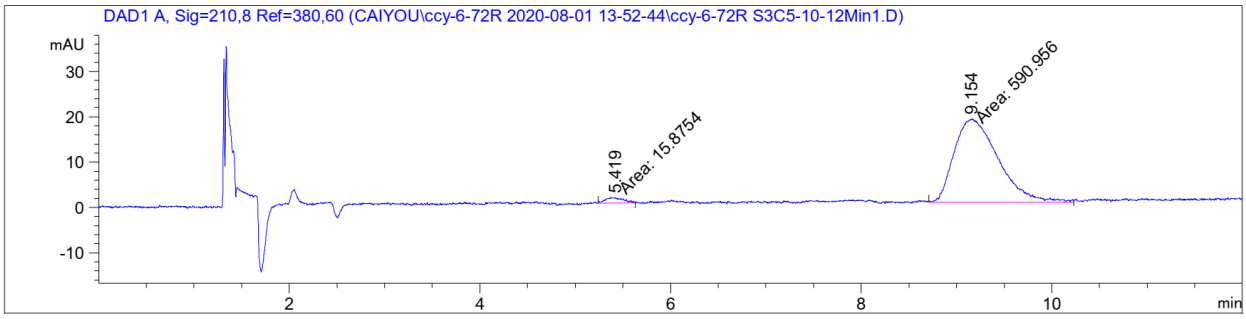


Figure 3, entry 50, (*S*,*S*)-**N1***: 94% ee; (*R*,*R*)-**N1***: 95% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.302	BB	0.1817	1358.63171	116.82149	97.1795
2	8.938	MM	0.4413	39.43311	1.48926	2.8205



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.419	MM	0.2074	15.87545	1.27601	2.6161
2	9.154	MM	0.5366	590.95599	18.35546	97.3839

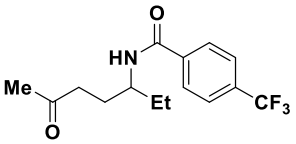
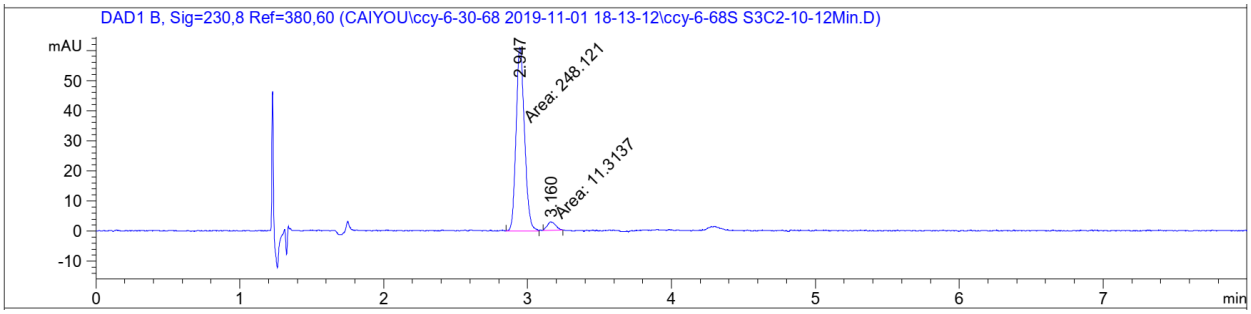
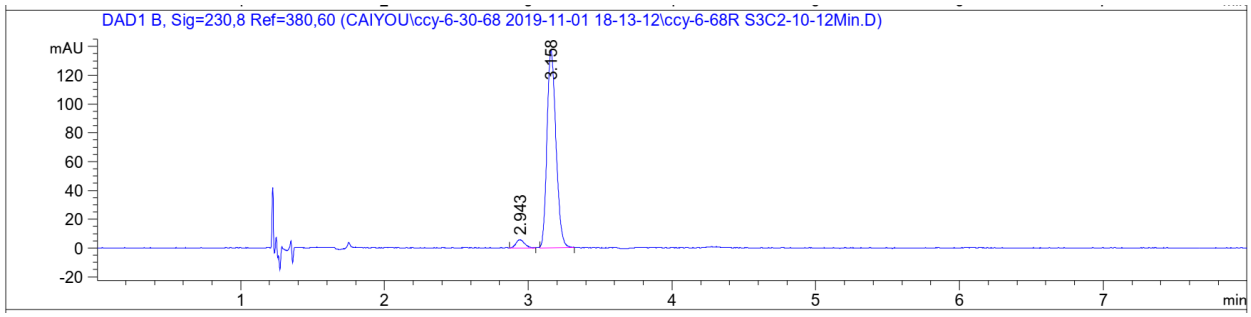


Figure 3, entry 51, (*S*,*S*)-**N1***: 91% ee; (*R*,*R*)-**N1***: 92% ee.



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.947	MM	0.0679	248.12097	60.87277	95.6391
2	3.160	MM	0.0685	11.31367	2.75251	4.3609



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.943	BB	0.0617	23.21696	5.67259	3.7393
2	3.158	BB	0.0677	597.67767	137.39816	96.2607

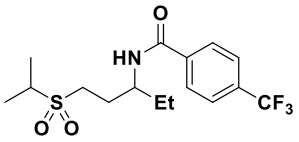
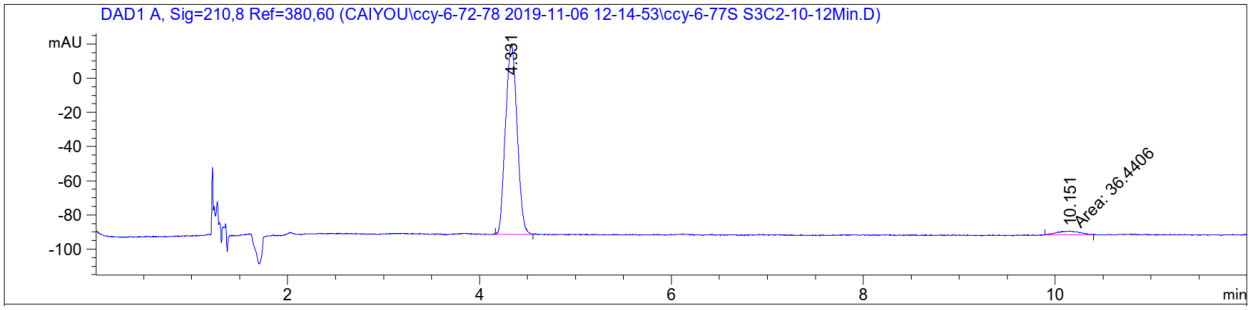
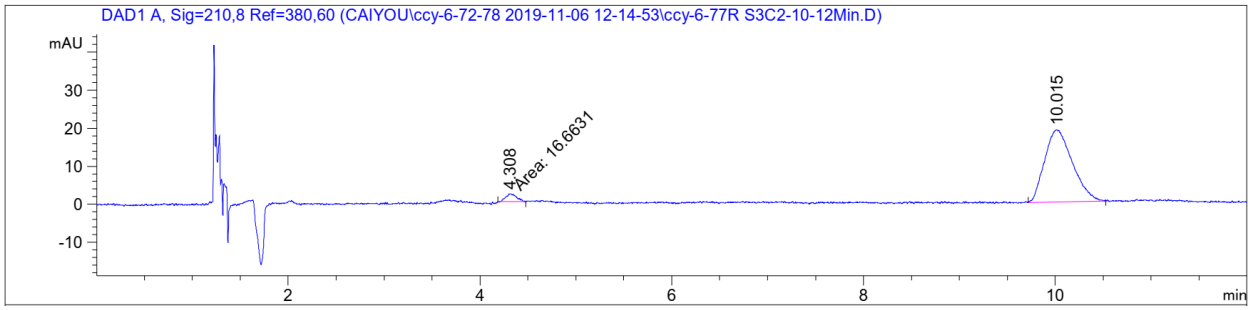


Figure 3, entry 52, (*S*,*S*)-**N1***: 92% ee; (*R*,*R*)-**N1***: 92% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.331	BB	0.1268	932.55444	111.21095	96.2393
2	10.151	MM	0.2703	36.44059	2.24656	3.7607



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.308	MM	0.1338	16.66306	2.07620	4.1932
2	10.015	BB	0.2411	380.72034	18.97305	95.8068

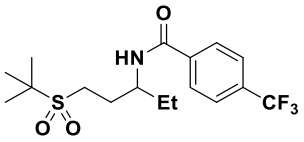
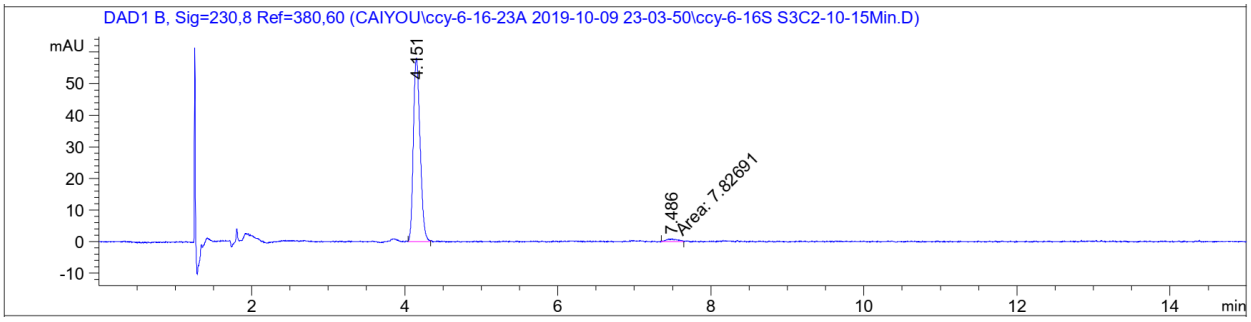
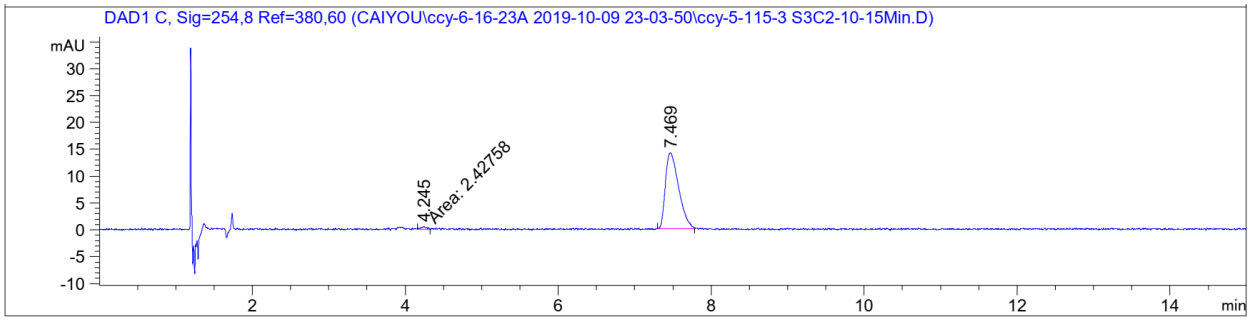


Figure 3, entry 53, (*S*,*S*)-**N1***: 96% ee; (*R*,*R*)-**N1***: 97% ee.



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.151	BB	0.0943	354.39502	57.96880	97.8392
2	7.486	MM	0.1599	7.82691	8.15768e-1	2.1608



Signal 3: DAD1 C, Sig=254,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.245	MM	0.0864	2.42758	4.68030e-1	1.3994
2	7.469	BB	0.1488	171.04861	14.16959	98.6006

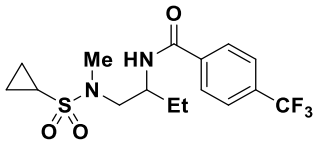
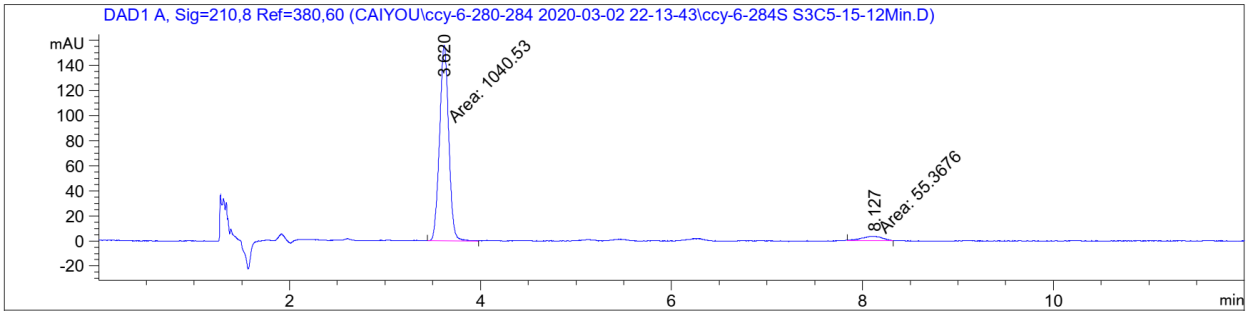
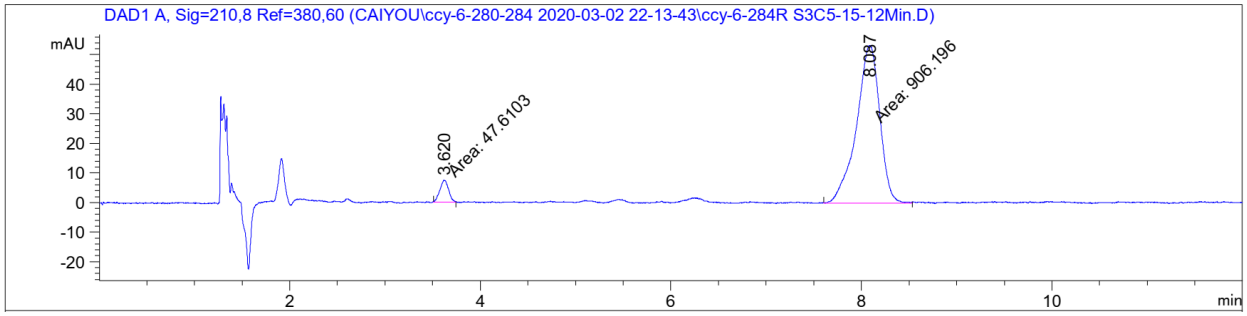


Figure 3, entry 54, (*S,S*)-**N1***: 90% ee; (*R,R*)-**N1***: 90% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.620	MM	0.1113	1040.53027	155.75165	94.9477
2	8.127	MM	0.2539	55.36756	3.63404	5.0523



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.620	MM	0.1069	47.61028	7.41968	4.9916
2	8.087	MM	0.2834	906.19556	53.28833	95.0084

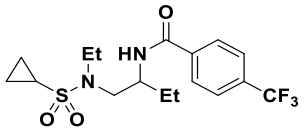
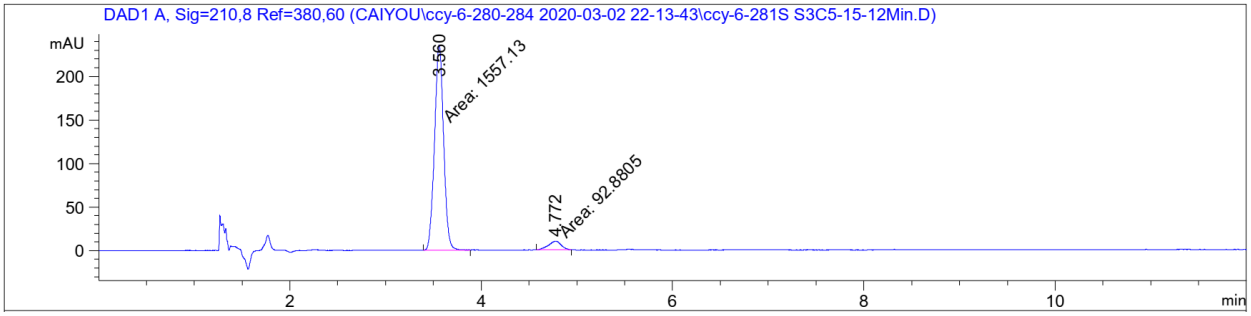
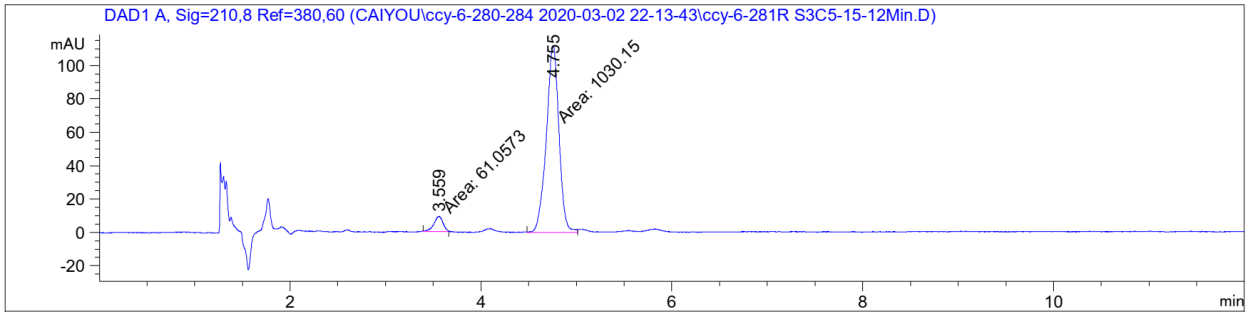


Figure 3, entry 55, (*S,S*)-**N1***: 89% ee; (*R,R*)-**N1***: 89% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.560	MM	0.1101	1557.13428	235.67030	94.3709
2	4.772	MM	0.1559	92.88049	9.92800	5.6291



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.559	MM	0.1113	61.05725	9.14283	5.5954
2	4.755	MF	0.1534	1030.15295	111.95043	94.4046

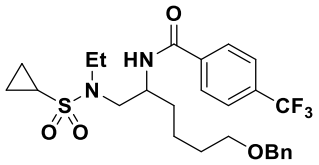
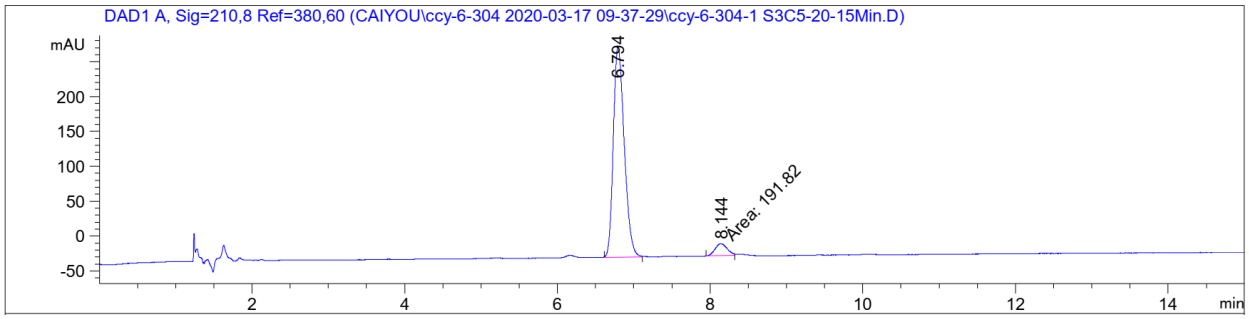
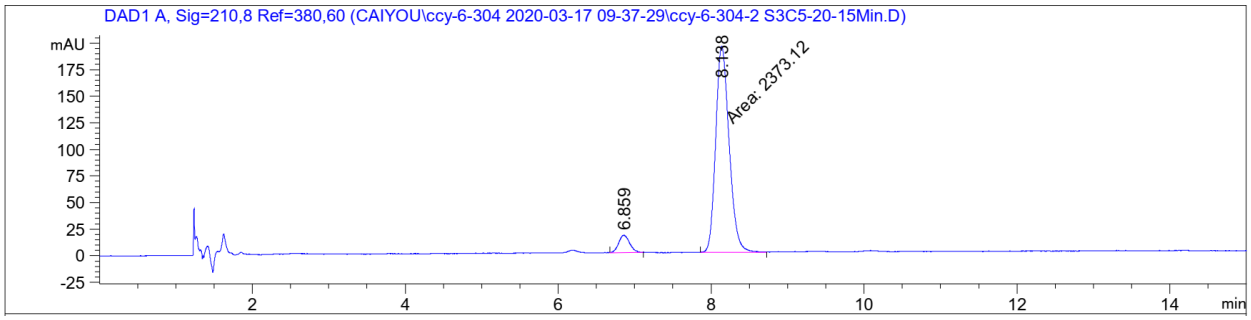


Figure 3, entry 56, (*S,S*)-**N1***: 88% ee; (*R,R*)-**N1***: 87% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.794	BB	0.1527	2993.82690	301.90152	93.9786
2	8.144	MM	0.1854	191.81963	17.24134	6.0214



Signal 3: DAD1 C, Sig=254,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.857	MM	0.1642	36.50961	3.70526	6.3801
2	8.138	MM	0.2034	535.73407	43.90274	93.6199

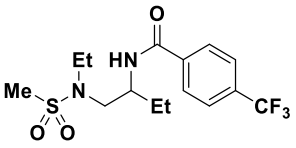
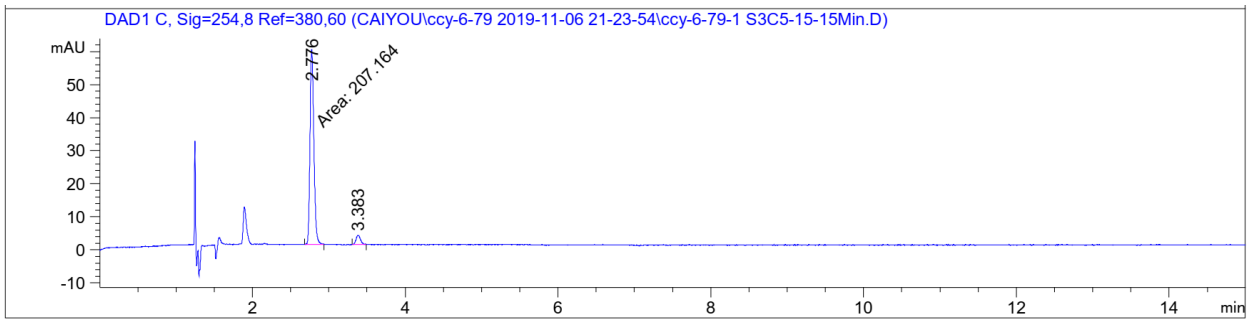
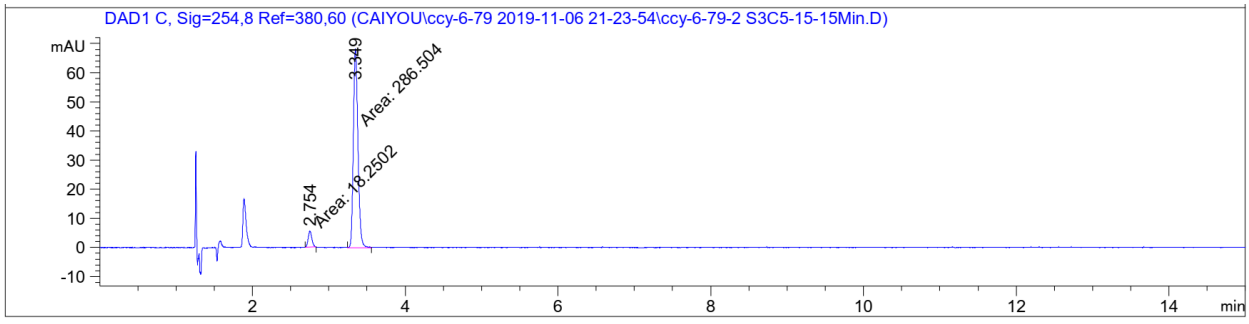


Figure 3, entry 57, (*S,S*)-**N1***: 89% ee; (*R,R*)-**N1***: 88% ee.



Signal 3: DAD1 C, Sig=254,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.776	MM	0.0585	207.16418	59.02166	94.6448
2	3.383	BB	0.0614	11.72187	2.82700	5.3552



Signal 3: DAD1 C, Sig=254,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.754	MM	0.0559	18.25024	5.43946	5.9885
2	3.349	MM	0.0698	286.50443	68.42720	94.0115

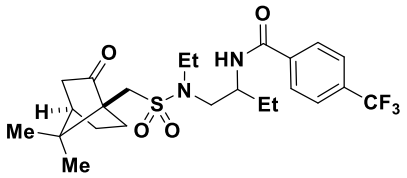
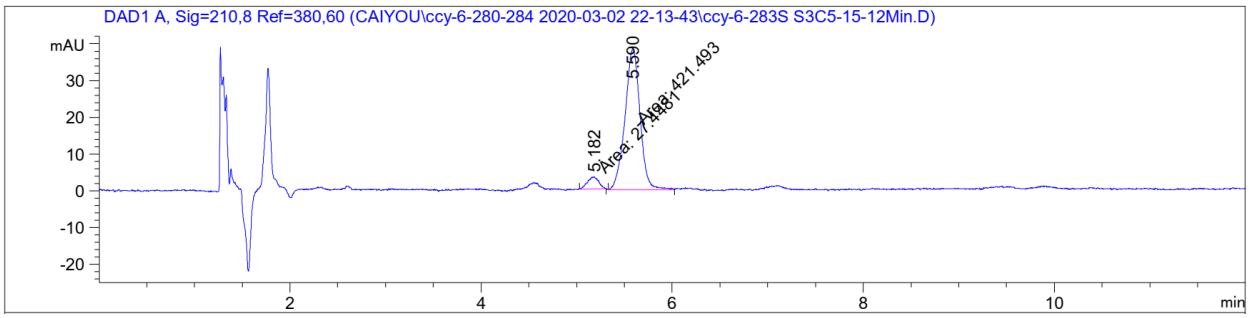
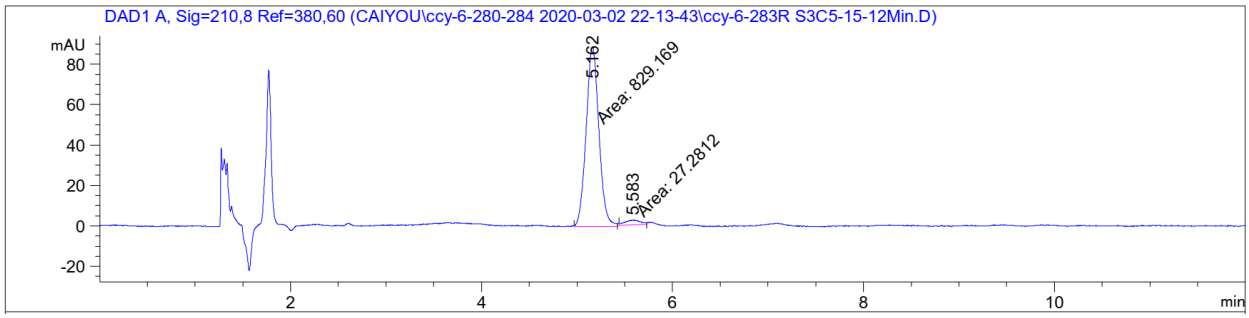


Figure 3, entry 58, (*S,S*)-**N1***: 6:94 dr; (*R,R*)-**N1***: 97:3 dr.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.182	MM	0.1388	27.44808	3.29635	6.1140
2	5.590	MM	0.1830	421.49310	38.38732	93.8860



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.162	MM	0.1553	829.16949	89.00712	96.8146
2	5.583	MM	0.1923	27.28115	2.36496	3.1854

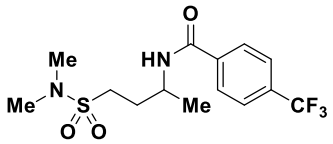
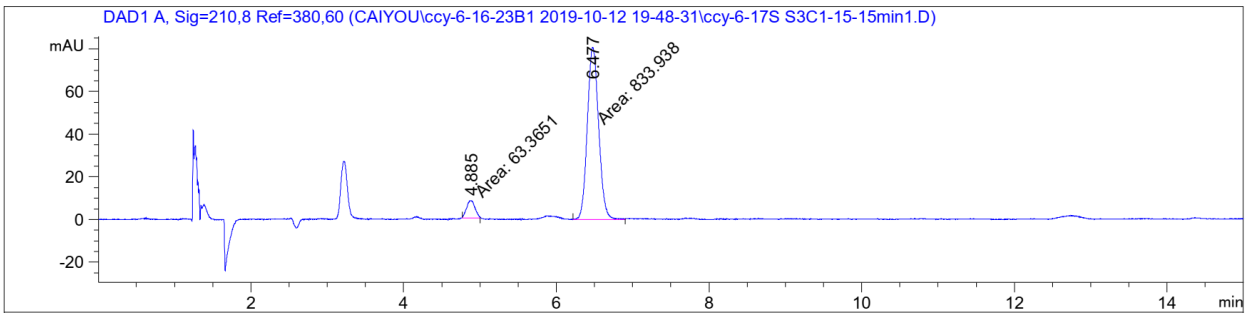
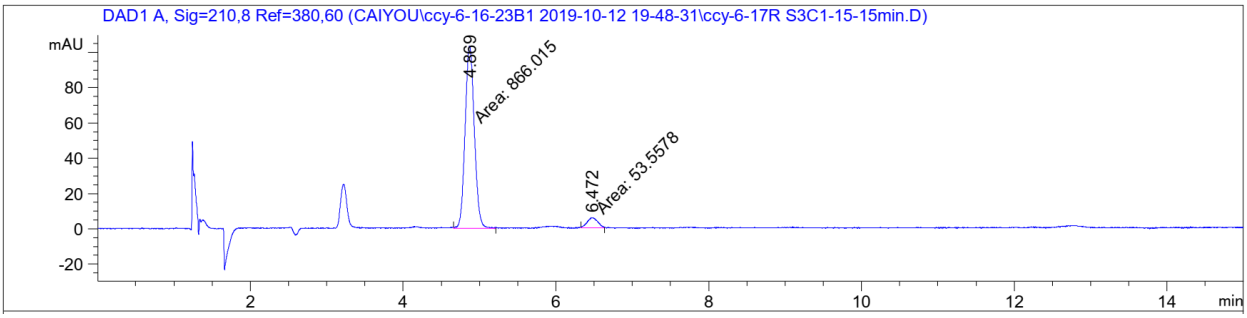


Figure 3, entry 59, (*S*,*S*)-**N1***: 88% ee; (*R*,*R*)-**N1***: 89% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.869	MM	0.1145	4.13093	6.01067e-1	6.1753
2	6.476	MM	0.1777	62.76347	5.88671	93.8247



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.869	MM	0.1400	280.19360	33.35794	94.7185
2	6.471	MM	0.1478	15.62370	1.76193	5.2815

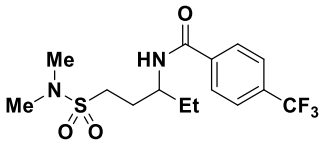
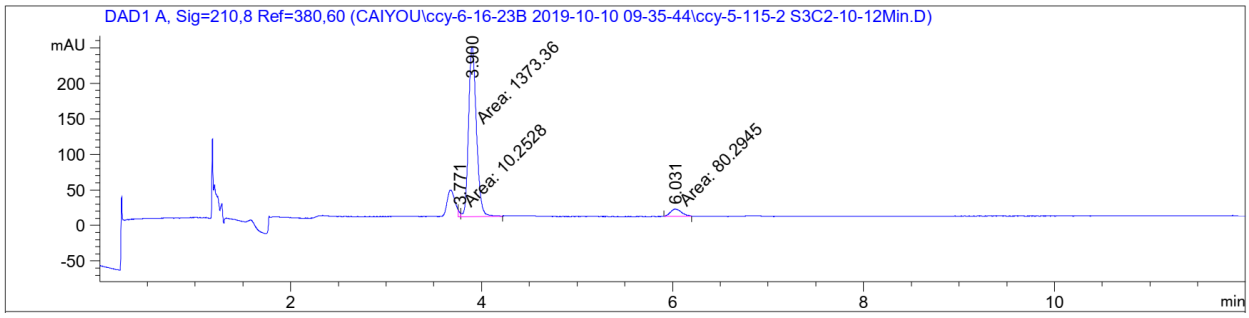
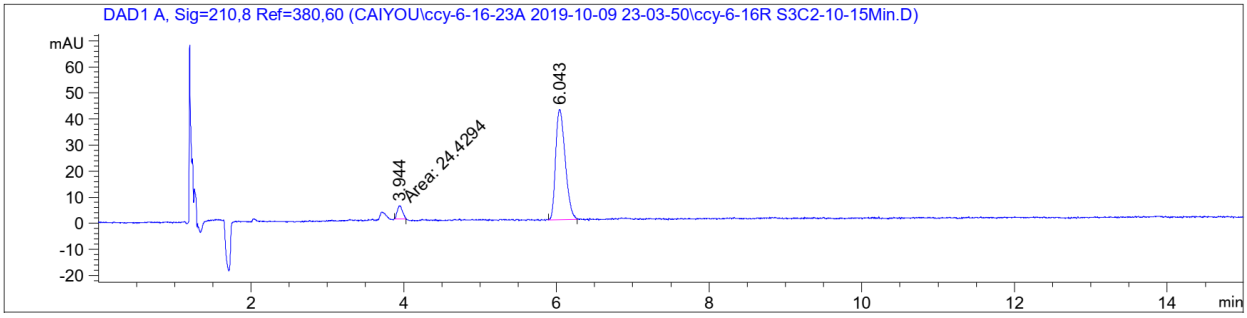


Figure 3, entry 60, (*S*,*S*)-**N1***: 89% ee; (*R*,*R*)-**N1***: 88% ee.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.900	VB	0.0864	438.23123	78.19644	94.4123
2	6.018	MM	0.1318	25.93624	3.28072	5.5877



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.961	MM	0.0767	1.80745	3.92885e-1	6.1788
2	6.044	MM	0.1510	27.44489	3.02886	93.8212

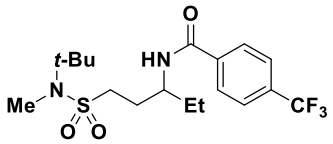
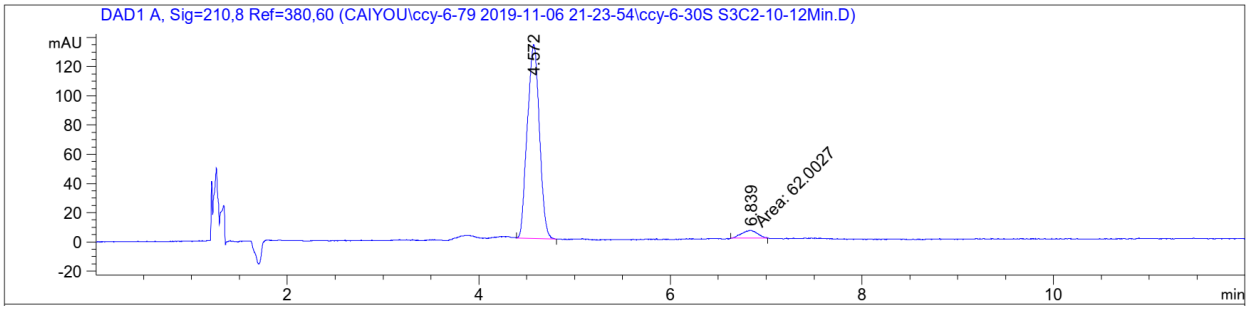
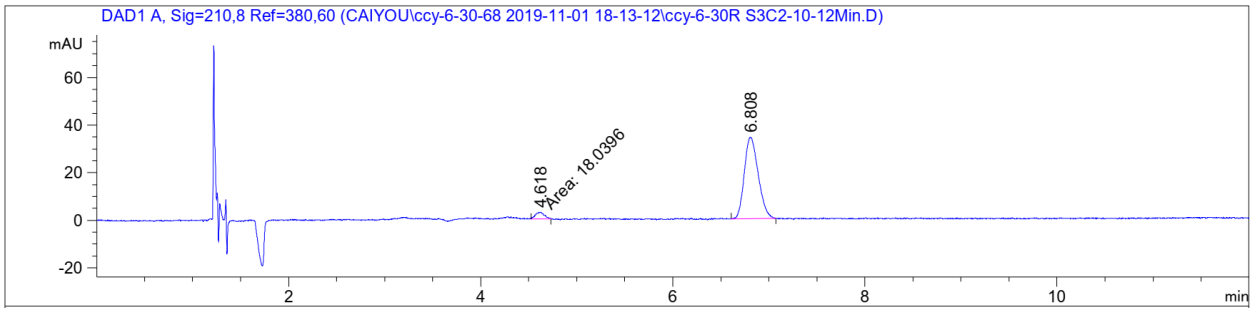


Figure 3, entry 61, (*S*,*S*)-**N1***: 90% ee; (*R*,*R*)-**N1***: 90% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.572	BB	0.1306	1166.18298	132.66771	94.9517
2	6.839	MM	0.1945	62.00266	5.31180	5.0483



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.618	MM	0.1065	18.03964	2.82267	4.9878
2	6.808	BB	0.1486	343.63693	34.10192	95.0122

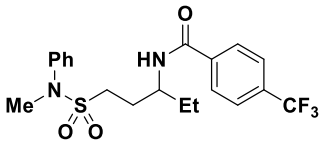
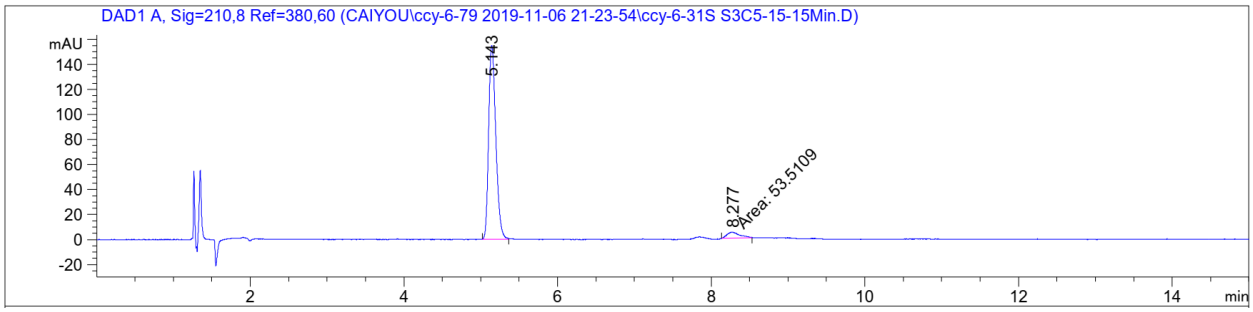
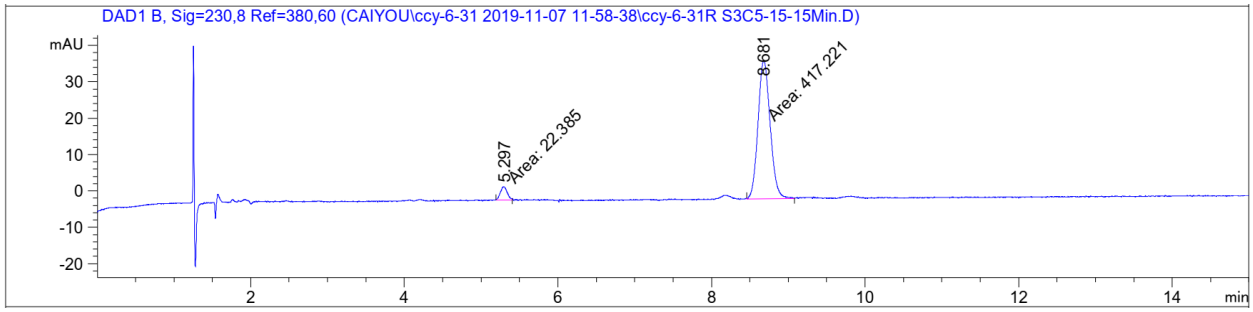


Figure 3, entry 62, (*S*,*S*)-**N1***: 90% ee; (*R*,*R*)-**N1***: 90% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.143	BB	0.0973	998.23889	154.61227	94.9122
2	8.277	MM	0.1891	53.51094	4.71550	5.0878



Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.297	MM	0.1041	22.38499	3.58443	5.0921
2	8.681	MM	0.1830	417.22079	37.99046	94.9079

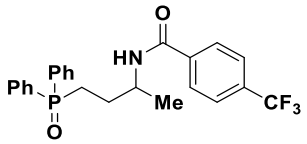
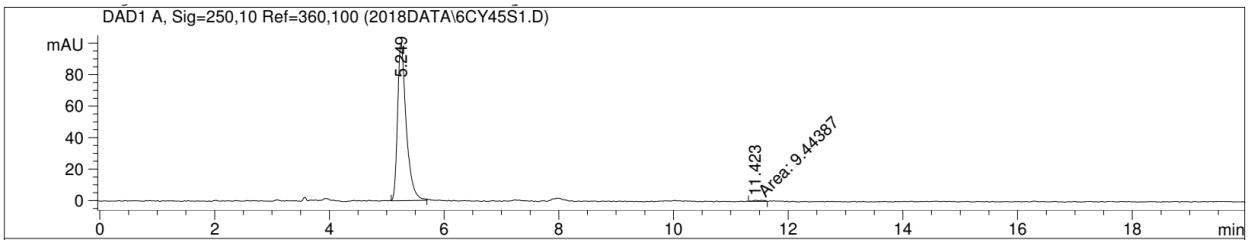
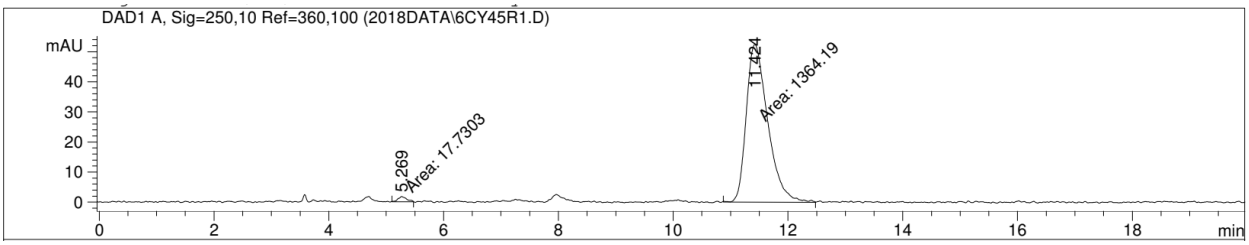


Figure 3, entry 63, (*S,S*)-**N1***: 98% ee; (*R,R*)-**N1***: 98% ee.



Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.249	BB	0.1589	1053.05566	99.95309	99.1112
2	11.423	MM	0.2153	9.44387	7.31219e-1	0.8888



Signal 4: DAD1 D, Sig=230,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.267	MM	0.1791	64.61309	6.01343	1.1834
2	11.418	MM	0.4405	5395.49609	204.15289	98.8166

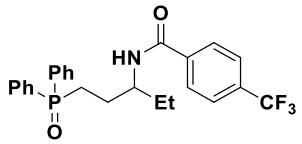
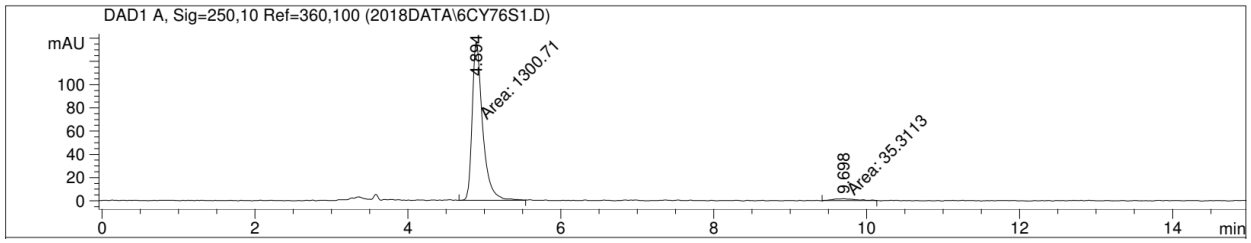
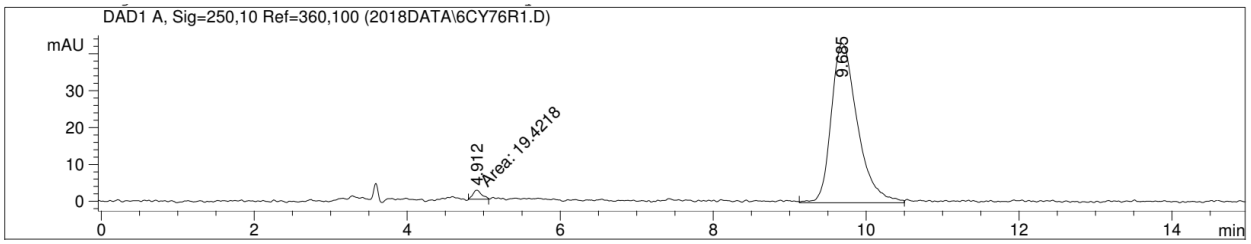


Figure 3, entry 64, (*S,S*)-**N1***: 95% ee; (*R,R*)-**N1***: 96% ee.



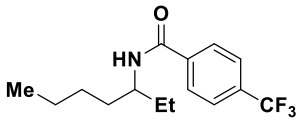
Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.894	MM	0.1588	1300.70654	136.48405	97.3570
2	9.698	MM	0.3561	35.31133	1.65265	2.6430

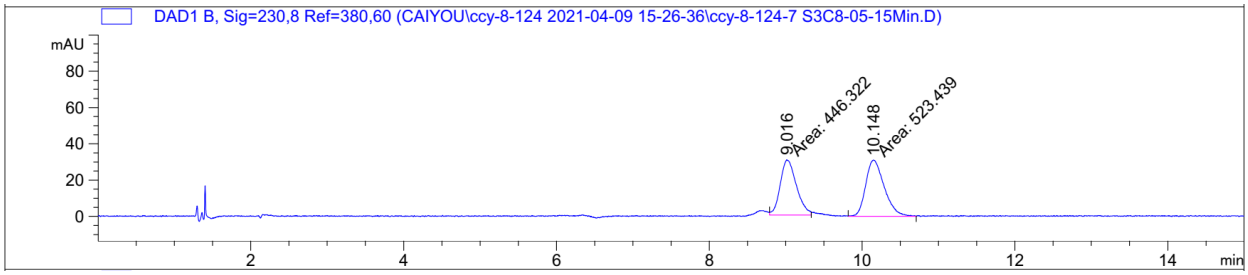


Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.912	MM	0.1345	19.42177	2.40744	1.8578
2	9.685	BV	0.3371	1026.01147	43.19157	98.1422

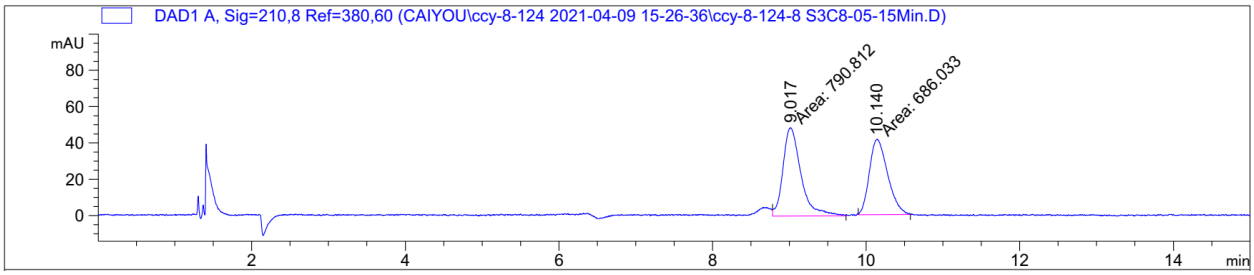


(*S, S*)-**N1***: 8% ee; (*R, R*)-**N1***: 8% ee.



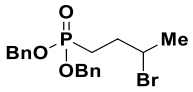
Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.017	MM	0.2398	557.20801	38.73314	46.1303
2	10.148	BB	0.2067	650.69354	39.40112	53.8697
Totals :				1207.90155	78.13427	

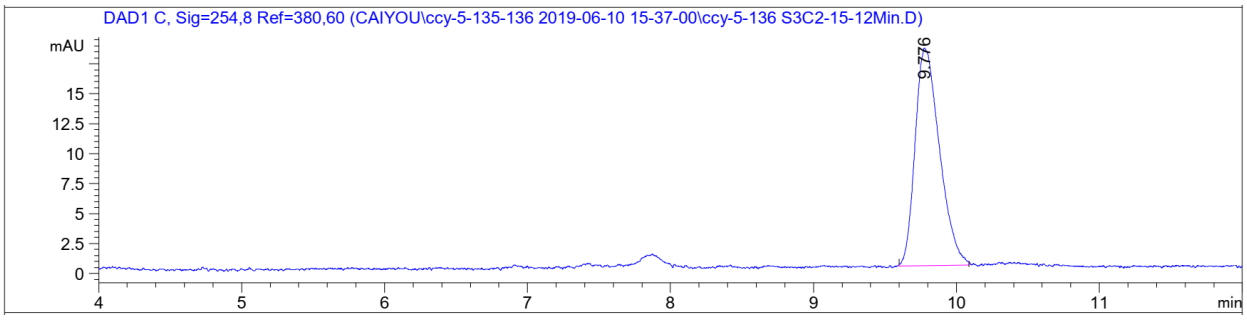


Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.016	MM	0.2747	619.83954	37.60752	53.8552
2	10.141	MM	0.2753	531.09863	32.15669	46.1448
Totals :				1150.93817	69.76421	

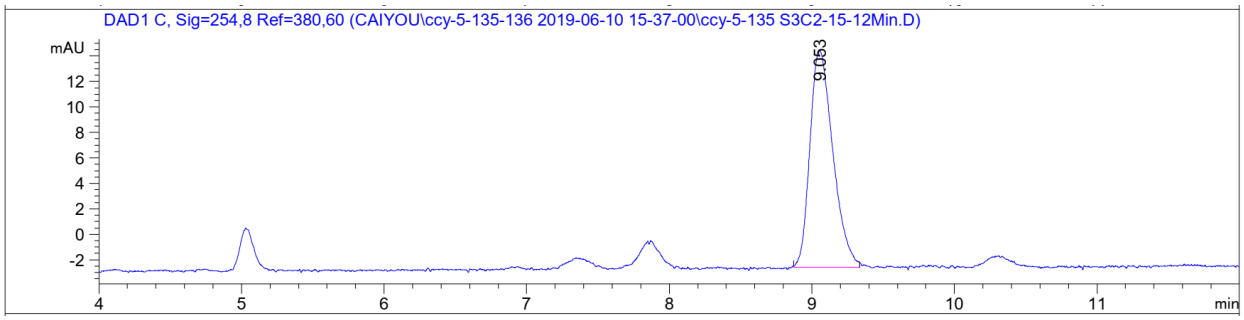


(*S*) > 99% ee; (*R*) > 99% ee.



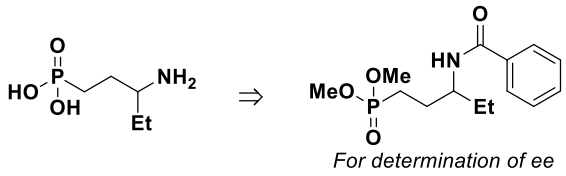
Signal 3: DAD1 C, Sig=254,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.776	BB	0.1644	215.79297	18.18751	100.0000

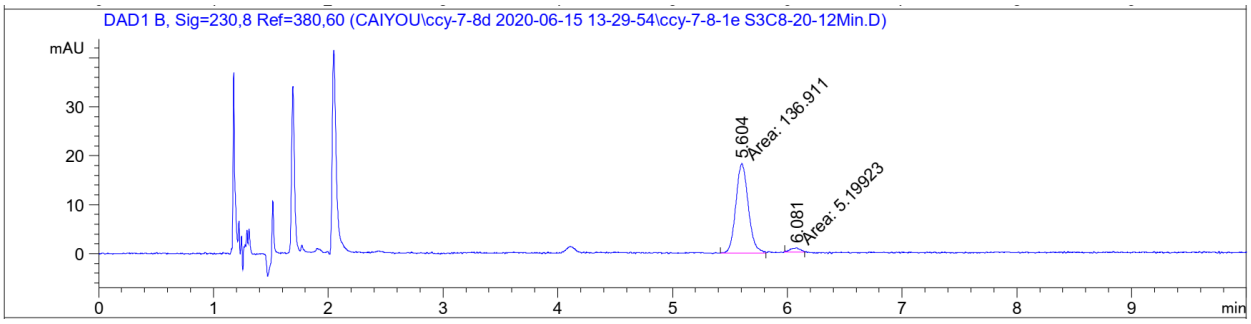


Signal 3: DAD1 C, Sig=254,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.053	BB	0.1703	190.47116	17.05728	100.0000

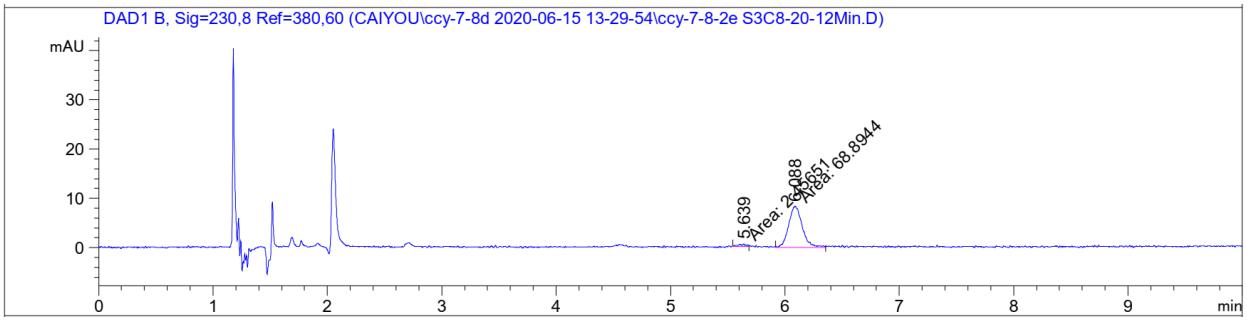


(*S,S*)-**N1***: 93% ee; (*R,R*)-**N1***: 93% ee.



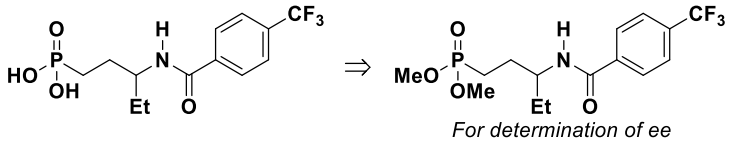
Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.604	MM	0.1250	136.91077	18.24758	96.3414
2	6.081	MM	0.0957	5.19923	9.05811e-1	3.6586



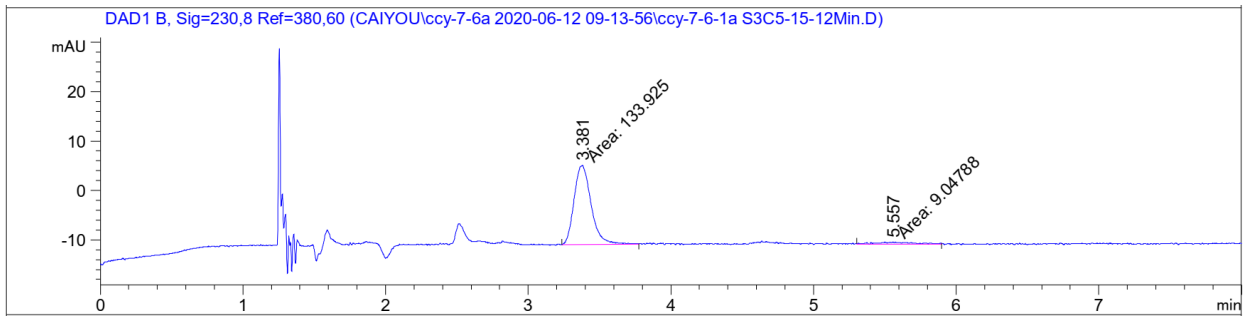
Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.639	MM	0.0787	2.45651	5.19940e-1	3.4429
2	6.088	MM	0.1364	68.89436	8.41688	96.5571

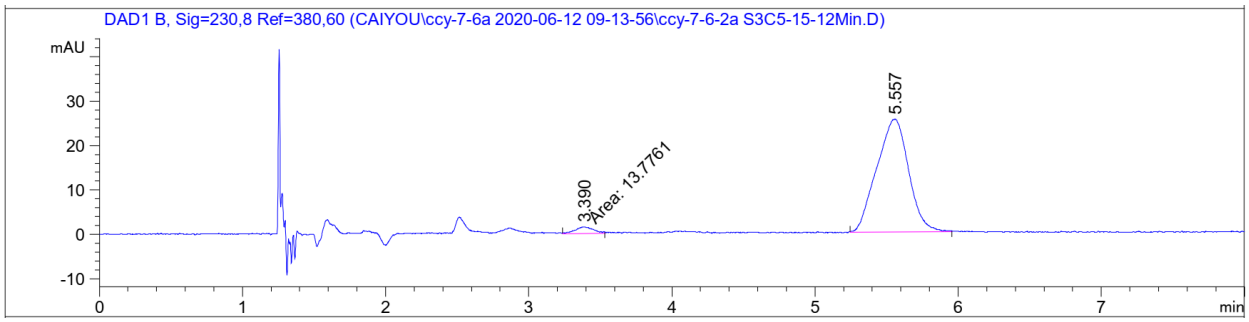


For determination of ee

(*S,S*)-**N1***: 93% ee; (*R,R*)-**N1***: 93% ee.

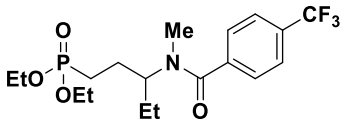


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.382	MM	0.1407	51.53800	6.10482	96.7423
2	5.557	MM	0.1421	1.73549	2.03579e-1	3.2577

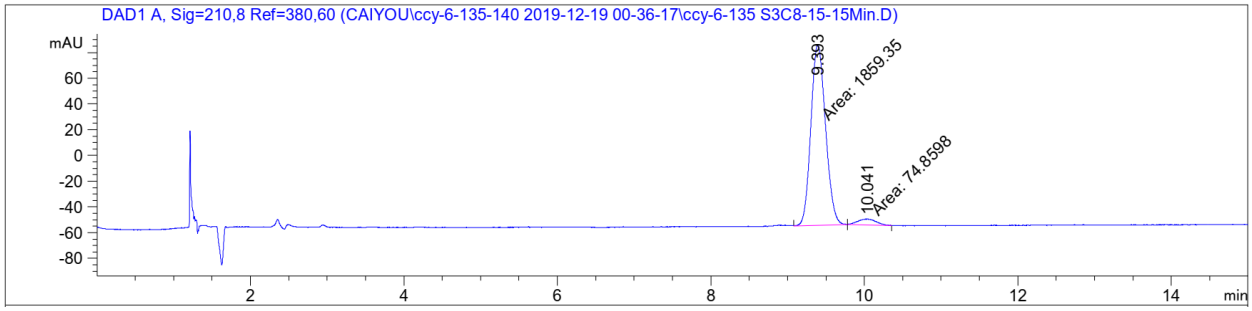


Signal 2: DAD1 B, Sig=230,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.390	MM	0.1507	13.77607	1.52350	3.3836
2	5.557	BB	0.2017	393.36990	25.39983	96.6164

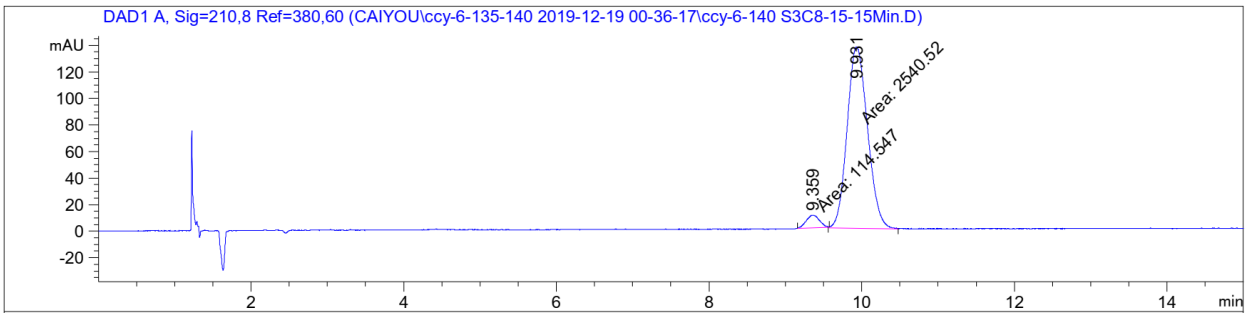


(*S*,*S*)-**N1***: 92% ee; (*R*,*R*)-**N1***: 92% ee.

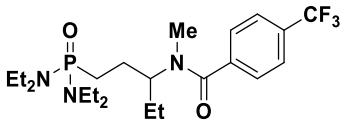


Signal 1: DAD1 A, Sig=210,8 Ref=380,60

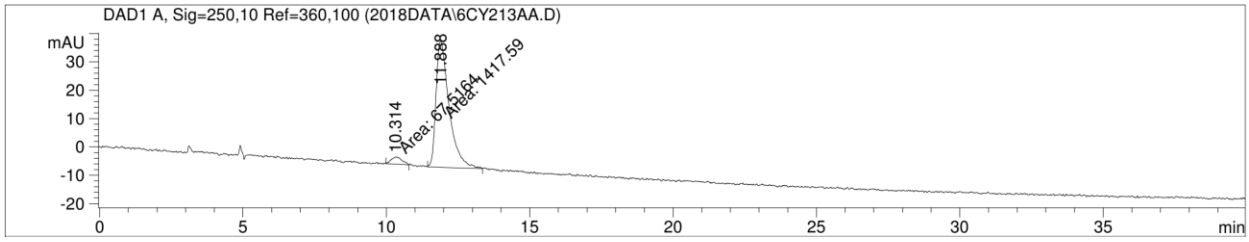
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.393	MM	0.2207	1859.34741	140.44455	96.1297
2	10.041	MM	0.2729	74.85979	4.57240	3.8703



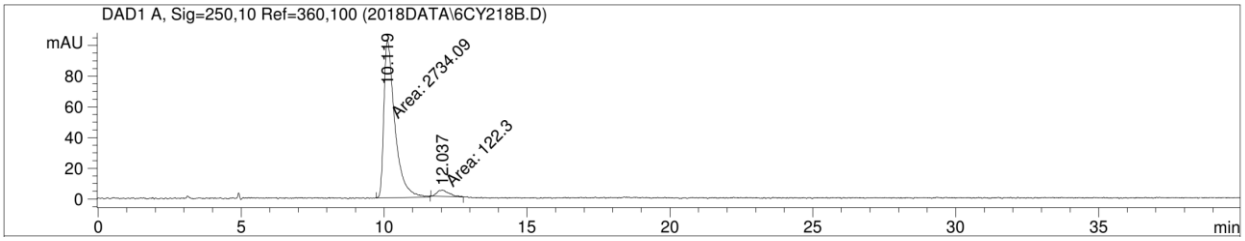
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.359	MM	0.1941	25.60907	2.19911	4.2882
2	9.931	MM	0.3114	571.59326	30.58783	95.7118



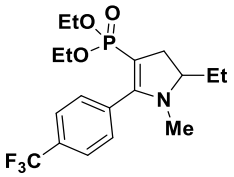
(*S,S*)-**N1***: 91% ee; (*R,R*)-**N1***: 91% ee.



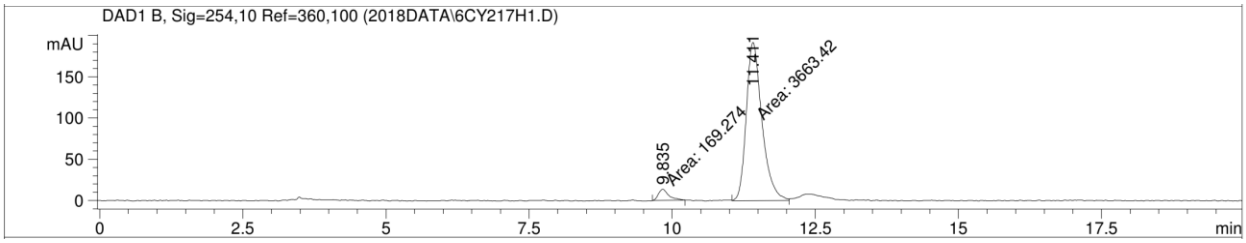
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.313	MM	0.4376	53.23878	2.02759	4.1732
2	11.885	MM	0.5227	1222.49768	38.97953	95.8268



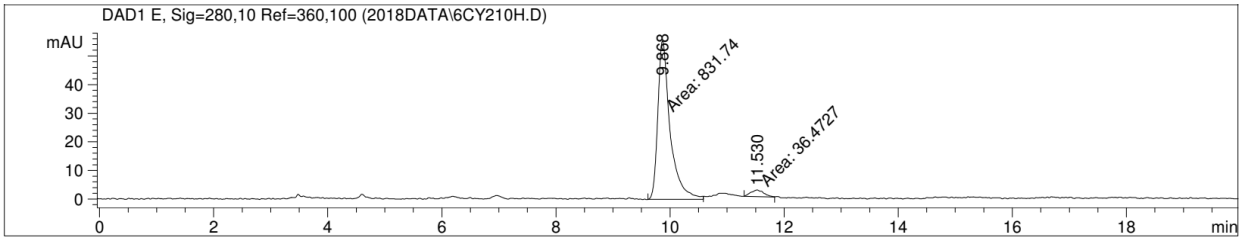
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.119	MM	0.4454	2734.08984	102.29945	95.7184
2	12.037	MM	0.5011	122.30002	4.06789	4.2816



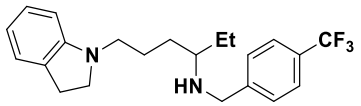
(*S,S*)-**N1***: 91% ee; (*R,R*)-**N1***92% ee.



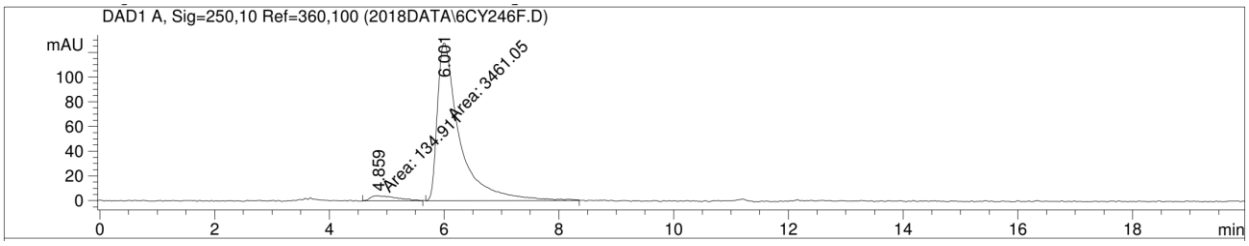
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.835	MM	0.2078	169.27351	13.57503	4.4166
2	11.411	MM	0.3182	3663.42139	191.89832	95.5834



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.868	MM	0.2502	831.74036	55.40158	95.7991
2	11.530	MM	0.2598	36.47271	2.33940	4.2009

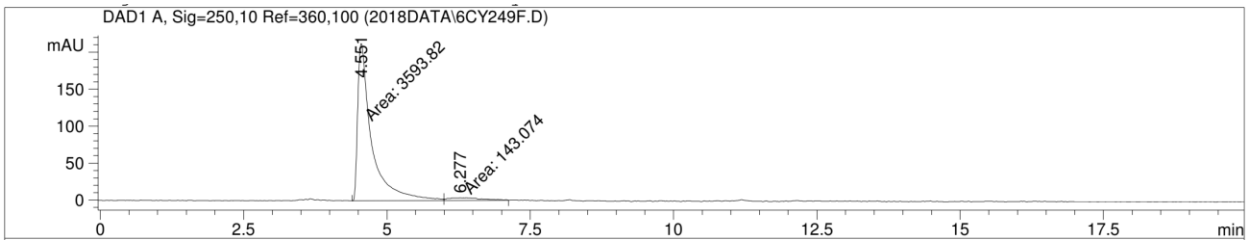


(*S,S*)-**N2***: 93% ee; (*R,R*)-**N2***: 92% ee.



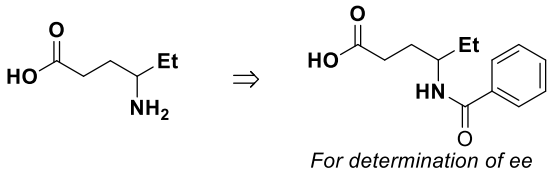
Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.859	MM	0.5342	134.91071	4.20926	3.7517
2	6.001	MM	0.4517	3461.05078	127.71568	96.2483



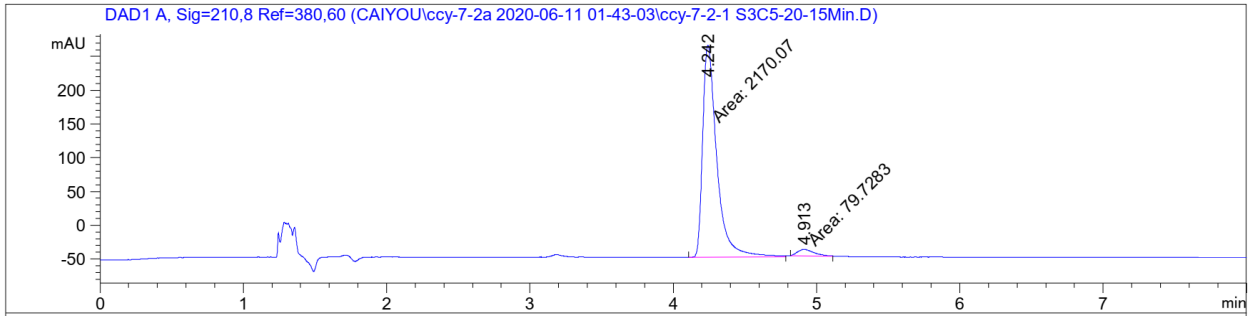
Signal 1: DAD1 A, Sig=250,10 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.551	MF	0.2815	3593.81616	212.74673	96.1713
2	6.277	FM	0.6662	143.07442	3.57931	3.8287



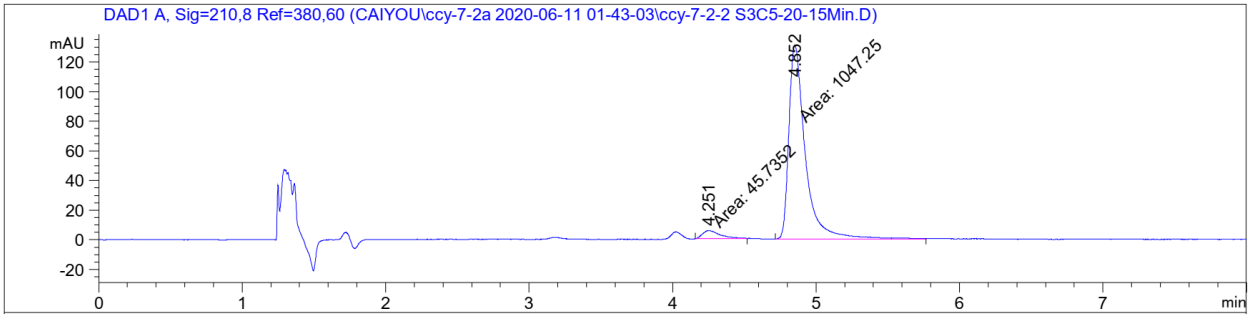
For determination of ee

(*S,S*)-**N2***: 93% ee; (*R,R*)-**N2***: 92% ee.



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.242	MM	0.1151	2170.07373	314.29648	96.4562
2	4.913	MM	0.1358	79.72826	9.78175	3.5438



Signal 1: DAD1 A, Sig=210,8 Ref=380,60

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.251	MM	0.1415	45.73516	5.38861	4.1844
2	4.852	MM	0.1334	1047.25159	130.87468	95.8156

XII. References

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